

Rebeka Rudolf^{1,2}, Mohammed Shariq^{1,3}, Urban Ferčec⁴, Alojz Križman¹, Peter Majerič^{1,2}

¹Univerza v Mariboru / University of Maribor, Fakulteta za strojništvo / Faculty of Mechanical Engineering,
Smetanova 17, 2000 Maribor, Slovenija, / Slovenia

²Zlatarna Celje d.o.o., Kersnikova 19, 3000 Celje, Slovenija / Slovenia

³Indian Institute of Technology (ISM), Dhanbad, Jharkhand 826 004, Indija / India

⁴Univerza v Ljubljani / University of Ljubljana, Fakulteta za kemijo in kemijsko tehnologijo / Faculty of Chemistry and Chemical
Technology, 1000 Ljubljana, Slovenija / Slovenia

Nanotehnologija v metalurgiji: analiza stanja in napoved razvoja

Nanotechnology in metallurgy: Status analysis and prediction of development

Povzetek

Napredek v metalurgiji je v drugi polovici dvajsetega stoletja povezan s hitro zamenjavo osnovnih proizvodnih sistemov; rečemo lahko, da gre za obdobje nove tehnične revolucije. V teh okvirih so poznane modifikacije elektro-talilnih sistemov, uvedba novih postopkov toplotnih obdelav jekel in vakuumskega pretaljevanja, kontinuirnega litja, kakor tudi metalurgija prahov in hidro-ekstrudiranje. Vse to predstavlja nove pristope za izdelavo visoko kakovostnih jekel.

V zadnjem desetletju je bil dosežen še napredok v metalurgiji predvsem z razvojem nanotehnologije, zlasti na področju proizvodnje visoko kakovostnih materialov za uporabo v elektroniki, optiki, gradbeništvu, energetiki, proizvodnji, astronautiki in drugod. V »metalurgiji na veliko« se tako že uporabljajo nekateri principi nanotehnologije, in sicer v postopkih za doseglo velike plastične deformacije v ustreznom orodju (v zaprtih matricah in zaprtih valjčnih žlebičih) ali pri termo redukciji z visoko stopnjo redukcije oziroma pri nizkotemperaturni finalni deformaciji. Nasprotno temu je nanotehnologija manj pomembna v metalurgiji železnih kovin. Trenutno se serijska proizvodnja kakovostnih valjanih jekel še vedno opira na legiranje. Stroški izdelave takšnih finozrnatih jekel brez vsebnosti oksidov in ostalih nekovinskih vključkov so visoki. Jeklo, ki ima drobnozrnatno mikrostrukturo, je namreč bistveno kakovostnejše, saj pomeni posredno garancijo za visoko trdnost, stabilnost pri nizkih/visokih temperaturah in odpornost proti koroziji. Konkurenčnost metalurških izdelkov na svetovnem trgu je prvenstveno odvisna od teh lastnosti jekel, saj omogoča uporabo le-teh za najrazličnejše aplikacije. Ob upoštevanju, da so med uporabo ta jekla različno obremenjena in ob tem izpostavljena velikim plastičnim deformacijam, je prisotnost defektov in različnih vključkov v mikrostrukturi neželena, saj lahko to pripelje do zloma materiala oziroma konstrukcije, prej kot je bilo predvideno. Zato je potrebno poznavati možne scenarije življenske dobe tovrstnih izdelkov. Za izračune življenske dobe se v zadnjem času uporablja simulacija na osnovi nanostrukturiranja. Pri tem se izračunavajo trdnosti posameznih nanofaz v conah maksimalnih napetosti z izbrano fragmentacijo matrične faze. Izračuni kažejo, da je trdnost in življenska doba takšnega izdelka odvisna od njegove začetne strukture in dinamično-struktturnih sprememb, kakor tudi od samoorganizacije utrjanja nanokompozitnih faz, ki razpršijo vneseno energijo. Urejen nanokompozit ima bistveno boljše lastnosti: trdoto, trdnost ter plastičnost v primerjavi z neurejenim. Z reguliranjem nastanka finozrnate strukture omogočamo nastanek urejenega nanokompozita, ki ni samo trden, ampak tudi plastičen in preoblikovalen v hladnem. To pa je osnova za poenostavitev postopka termo-mehanske obdelave tovrstnih jekel.

Zaključimo lahko, da je proces izdelave raznovrstnih jekel, vezan na doseganje drobnozrnate strukture z maksimalno vsebnostjo utrjevalne kovinske nanofaze (karbidi, nitridi, karbo-nitridi, intermetalne faze) in z minimalno vsebnostjo žvepla, fosforja, oksidov in ostalih nekovinskih vključkov. Danes se zdi, da je takšen nanosistemski pristop obravnavanja jekel zelo obetaven.

Ključne besede: metalurgija, nanotehnologija, utrjanje, simulacije

Abstract

Progress in metallurgy in the second half of the twentieth century is connected with the rapid replacement of basic production systems, and we can say that this is a period of a new technical revolution. Within these frameworks there are known modifications of electro-melting systems, introduction of new processes of heat treatment of steels and vacuum refining, continuous casting, as well as powder metallurgy and hydro-extrusion. All this represents new approaches for the production of high-quality steels. In the last decade, progress has been made in metallurgy, primarily through the development of nanotechnology, especially in the field of manufacturing high quality materials for use in Electronics, Optics, Construction, Energy, Manufacturing, Astronautics and elsewhere. Some of the principles of nanotechnology are already being used in the "metallurgy in bulk" procedures for achieving large plastic deformation in the appropriate tool (in closed matrices and closed rolling grooves) or in thermo-reduction with a high degree of reduction or in a low temperature final deformation. In contrast, nanotechnology is less important in metallurgy of ferrous metals. At present, the serial production of quality rolled steel still relies on alloying. The cost of producing such finely grained steels without oxides and other non-metal inclusions is high. Steel, which has a fine grain microstructure, is significantly better, because it represents an indirect guarantee for high strength, stability at low/high temperatures and resistance to corrosion. The competitiveness of metallurgical products on the world market depends primarily on these properties of steels, since it allows them to be used for a wide variety of applications. Taking into account that during use, these steels are subjected to varying stresses and are subjected to high plastic deformations, the presence of defects and various inclusions in the microstructure is undesirable, as this can lead to a breakdown of material or construction before its time. Therefore, it is necessary to know the possible scenarios of the life of such products. Simulation based on nanostructuring has recently been used for life-cycle calculations. In the simulations, the strengths of individual nanophases are calculated in the maximum tension zones with a selected matrix phase fragmentation. Calculations show that the strength and lifetime of such a product depends on its initial structure and dynamic-structural changes, as well as from the self-organisation of the hardening of nanocomposite phases that disperse the energy input. An ordered nanocomposite has significantly better properties hardness, strength and plasticity, compared to the unordered. By regulating the formation of a fine-grained structure, we allow the formation of an ordered nanocomposite which is not only solid, but also plastic and cold transformable. This is the basis for the simplification of the thermo-mechanical treatment of such steels.

We can conclude that the process of manufacturing of various steels is related to achieving a fine grain structure with a maximum content of hardening metal nanoparticles (carbides, nitrides, carbo nitrides, intermetallic phases) and with minimum sulphur,

phosphorus, oxide and other non-metallic inclusions. Today, this nanosystemic approach to the treatment of steels seems to be very promising.

Key words: metallurgy, nanotechnology, hardening, simulations

1 Uvod

Nanotehnologija je veja znanosti, ki se osredotoča na materiale z vsajeno dimenzijo pod 100 nm. Nanomateriali (nanodelci, nanocevke, nanopiramide) imajo drugačne lastnosti v primerjavi z materiali običajnih dimenzijs. Njihove spremenjene fizikalne in kemične lastnosti izhajajo iz velikega razmerja med površino in volumnom ter visoke površinske aktivnosti. Znane so različne metode izdelave nanodelcev, ki jih delimo na dva pristopa: od spodaj navzgor in od zgoraj navzdol. Primeri izdelave od spodaj navzgor so metode sol-gel, kemično naparjevanje, sinteza z razpršilnim plamenom, različne pirolize, ter atomska ali molekularna kondenzacija [1-4]. Med metode izdelave od zgoraj navzdol štejemo lasersko ablacijo, nanolitografijo in visoko-energijsko mletje [5, 6]. Trenutno te metode omogočajo proizvodnjo majhnih količin nanodelcev, z velikimi variacijami oblik in velikosti pri izdelavi različnih serij nanodelcev.

2 Sodobno stanje nanotehnologije v metalurgiji

Doseganje drobnozrnate strukture pri nastanku materiala na področju metalurgije je bilo vedno videti težavno in zahtevno [7]. Danes obstaja več obetavnih pristopov, ki temeljijo na nanotehnologiji. Trdnost kovin, zlasti jekel različnih razredov, se lahko poveča za faktor 3-4 z uporabo nano-stanj, poveča se trdota v hladnem, ob tem pa se zelo poveča še odpornost na korozijo [8, 9]. Glavna prednost nanotehnologije

1 Introduction

Nanotechnology is a branch of science and engineering focused on materials with at least one dimension below 100 nm. Nanomaterials (nanoparticles, nanotubes, nanopyrramids) have different properties compared to materials with ordinary dimensions. Their altered physical and chemical properties come from a large surface-to-volume ratio and a high surface activity. Different production methods for nanoparticles are known; they are divided into bottom-up and top-down approaches. Bottom-up examples include sol-gel, chemical vapour deposition, flame spray synthesis, various pyrolysis and atomic or molecular condensation [1-4]. Top-down methods include laser ablation, nanolithography and high-energy milling [5, 6]. Currently, these methods are suitable for production of small quantities of nanoparticles with major variations in shapes and sizes of the nanoparticles from production of different batches.

2 State-of-the-art Nanotechnology in Metallurgy

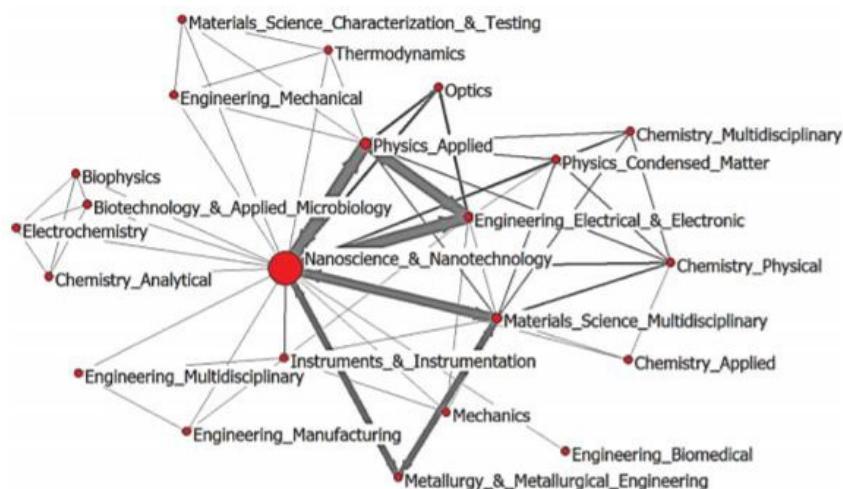
The production of a fine-grained structure in the formation of a material in the field of Metallurgy had always seemed tricky, difficult and challenging [7]. Today, several approaches based on Nanotechnology are promising. The strength of the metal, especially steels with different grades, can be increased by a factor of 3–4 with the application of nano-states, the hardness by an order of magnitude with the improvement

je mikro legiranje v fazah nitrida in karbo-nitrida pri jeklu, pa tudi pri širokem naboru kovinskih izdelkov. Nedavno so poročali o nano-procesih v kovinski talini, ki so bili ustvarjeni za izdelavo fino zrnate strukture z močnim povečanjem običajne trdnosti in trdnosti v hladnem pri poznanih ogljikovih ter nizko legiranih jeklih. Uvajanje teh novih nanotehnoloških metod je povečalo proizvodnjo takšnih jekel: 85-86 % celotne proizvodnje, vključno s 72-74 % ogljikovimi jekli in 13-14 % nizko legiranimi jekli [10]. Brez dvoma mora izdelava nove generacije kovinskih izdelkov temeljiti na kombinaciji nano-tehnoloških načel, vključno z nano-procesi za taljenje jekla, tlačne obdelave kovin in toplotne obdelave, s čimer se poveča tudi proizvodnja železniških koles in tirnic. Izboljšave pri razvoju tirnic s povečanjem njihove življenske dobe in zanesljivosti zahteva vključitev nanotehnološkega mikrolegiranja železniškega jekla z elementi, ki tvorijo karbo-nitridne elemente s pomočjo atomskega dušika in aluminija. Nedavna poročila so pokazala oblikovanje proizvodne tehnologije za čisto drobnozrnatno jeklo s samoorganizacijo utrditve nanofaz, ki predstavljajo novo stopnjo razvoja nano-sistemov v metalurgiji in tudi novo stopnjo razvoja proizvodne tehnologije za visoko kakovostna jekla. Za proizvodnjo vroče valjanega traku iz ogljikovega, nizko legiranega in manganovega jekla s povišano trdnostjo in stabilnostjo v hladnem zagotavljajo nanotehnologije visoko gospodarsko učinkovitost. Njihova uvedba ne zahteva kapitalskih izdatkov in ne vpliva na delovne pogoje ali na okolje. Metalurška podjetja, ki aktivno preučujejo uporabo nanotehnologij, imajo možnost uesti izdelke z izboljšanimi lastnostmi in zmanjšati proizvodne stroške z jasnimi konkurenčnimi koristmi [11].

in the cold strength, and great increase in the corrosion resistance [8, 9]. The main advantage of Nanotechnology is micro-alloying in the nitride and carbo-nitride phases in the case of steels, as well as in a wide range of metal products. Recently reported nano-processes during the metal melt have been created to produce a fine-grain structure with a sharp increase of the strength and cold strength in the widely used carbon and low-alloy steels. The significance of the introduction of these new nano-technological methods has increased the output of such steel: 85–86% of total production, including 72–74% of carbon steel and 13–14% of low-alloy steel [10]. Undoubtedly, the creation of a new generation of metal products must be based on a combination of nano-technological principles, including nano-processes for steel smelting, pressure treatment of metals, and heat treatment, thereby increasing the production of railroad wheels and rails. Improvement in the development of rails with an increase in their operational life and reliability calls for the incorporation of nano-technological micro-alloying of rail steel with carbo-nitride-forming elements by means of atomic nitrogen and aluminum. Recent reported works showed the creation of a production technology for pure fine-grain steel with self-organisation of strengthening nanophases, representing a new stage in the development of nano-systems in Metallurgy, and also a new stage in the development of a production technology for high quality steel. The production of hot-rolled strip from carbon, low-alloy, and manganese steel of elevated strength and cold stability, nanotechnologies ensure high economic efficiency. Their introduction does not require capital expenditure, and has no impact on the working conditions or on the environment. Metallurgical enterprises actively exploring the application of

Sl. 1: Mrežna struktura področij nanoznanosti in nanotehnologij

Fig. 1: Disciplinary network structure of Nanoscience & Nanotechnology



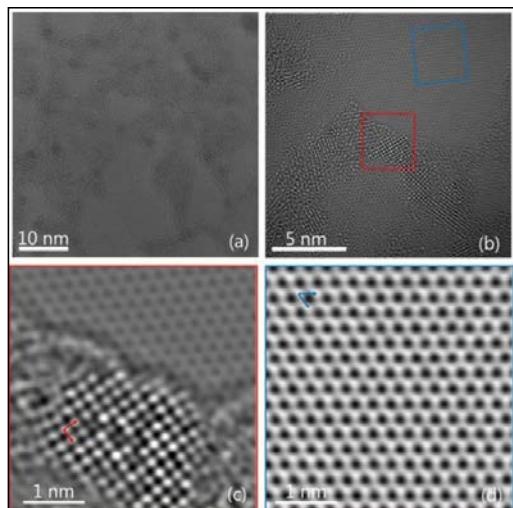
Vpogled v strukturo področij znanosti kaže osrednjo mesto za nanoznanost & nanotehnologije (glej sliko 1).

Na osnovi tega lahko sklepamo, da je nanoznanost, ki se je začela leta 1980, danes uvrščena v središče omrežja tehničnih znanosti. Nanoznanost in nanotehnologija je povezana z 22 vozlišči in je neizogibno vključena v vse vidike razvoja ter raziskav.

nanotechnologies have the opportunity of introducing products with improved properties and reducing production costs, with clear competitive benefits [11].

Insight into the Disciplinary Science Structure shows the central location of Nanoscience & Nanotechnology (see Figure 1).

It can be concluded that Nanoscience, which started in 1980, today, has a position within all technician science in the centre of the network. It looks as though Nanoscience



Sl. 2: (a) HR-TEM slika z velikim vidnim poljem, ki prikazuje velike 2 nm Ti-okside, (b) slika iz žariščne serije z izbranimi regijami za rekonstrukcijo izhodnih valov. Fazne slike rekonstruiranega vala, ki prikazujejo eno jedro in grafensko mrežo, so prikazane v slikah c in d [15]

Fig. 2: (a) HR-TEM image with a large field of view showing many 2 nm Ti-oxide, (b) One image from the focal series with the selected regions for exit-wave reconstruction. The phase images of the reconstructed wave showing one nucleus and the graphene lattice are shown in panels c and d [15]

3 Primer iz industrijske prakse

Eden izmed bolj znanih primerov povezave nanotehnologije z metalurgijo je proizvodnja zlitine Ti-Nb. Zlitina se je izdelala z različnimi vsebnostmi Nb, s procesom metalurgije prahov (Powder Metallurgy – PM), pri čemer so bile dobljene veliko boljše mikrostrukture in mehanske lastnosti. Pri eni od študij [12] so ocenili vpliv nastanka faz na mehansko trdnost Ti-Nb zlitine, izdelane s PM procesom.

Drugi primer je izdelava AlSiMnFe zlitine s pomočjo Equal Channel Angular Pressing (ECAP), kjer so v primerjavi s konvencionalnimi metodami pridobili popolnoma drugačne mikrostruktурne in mehanske lastnosti [13]. Z ECAP je bila stopnja deformacije zlitine določena za en prehod in z največjo obremenitvijo. Nano-finozrnato zlitino AlSiMnFe so izdelali z udobrnjevanjem zrnate žarjene zlitine z večkratnim ECAP postopkom pri sobni temperaturi. Rezultati navajajo dva režima: pri 1 do 2 prehodih se mikrostruktura razvije v nano-finozrnato, pri 2 do 4 prehodih pa se povprečna velikost zrn ne spremeni.

Naslednji primer je deklorinacija prahu cinkovega oksida z nano velikostjo s tehnologijo čiste metalurgije [14]. Postopek deklorinacije iz prahu cinkovega oksida z mikrovalovnim pečenjem so ocenili glede na učinek različnih temperatur za pečenje in glede na čas držanja. Rezultati raziskav so pokazali, da se ZnCl₂ in PbCl₂ z visokim faktorjem izgube prednostno segrejeta z mikrovalovi, delež dekloriranja pa lahko doseže 97,22 % po mikrovalovnem pečenju pri 650 °C za 40 minut.

Nadzorovana sinteza hibridnega nanomateriala na osnovi titanovega oksida in enoslojnega grafena (Single-Layer Graphene, SLG) z uporabo nanašanja atomskega sloja (Atomic Layer Deposition, ALD) je prav tako dober

& Nanotechnology are connected to the 22 nodes, and is necessarily included into all aspects of development and research.

3 Example from industrial praxis

One of the well-known examples of the connection of Nanotechnology and Metallurgy is the production of Ti-Nb Alloy at different compositions of Nb, produced via the Powder Metallurgy (PM) Route, where much better microstructures and mechanical properties were obtained. In one study [12] the effect was evaluated of phase formation to the mechanical strength of Ti-Nb alloy produced by the PM process.

The second example is the production of AlSiMnFe alloy by Equal Channel Angular Pressing (ECAP), where completely different microstructural and mechanical characteristics were obtained compared with conventional methods [13]. By ECAP, the defectiveness degree of the alloy was determined for one pass and maximum strain. Nano-fine grained AlSiMnFe alloy was produced by refining grained annealed bulk by multi-pass ECAP at room temperature. The results reveal two regimes: From 1 to 2 passes, the microstructure evolves to the equivalent of nano-fine grains, and from 2 to 4 passes there is no strict change in the average grain size.

The next example is the dechlorination from nano sized zinc oxide dust by clean metallurgy technology [14]. The process of dechlorination from zinc oxide dust by microwave roasting was evaluated considering the effect of different roasting temperatures and holding times. The research results showed that the ZnCl₂ and PbCl₂ with high-loss factor were heated preferentially by microwave, and the dechlorination rate can reach 97.22% after microwave roasting at 650°C for 40 min.

primer pri načrtovanju metalurškega procesa [15]. Morfologijo in kristaliničnost oksidnega sloja na SLG lahko kontroliramo predvsem s temperaturo nanašanja, pri čemer dosežemo bodisi enotno amorfno plast pri 60°C ali ~2 nm posameznih nanokristalov na SLG pri 200°C po samo 20 ciklusih ALD (glej sliko 2). Nепrekinitена в еднакомерна аморфна пласт, обlikovана на SLG по 180 циклисах при 60°C, се лагко претвори в поликристалинична пласт, ки вsebuje domene faze anataza TiO₂ po nanašanju z žarjenjem при 400°C v vakuumu. Z uporabo presevne elektronske mikroskopije s korigirano aberacijo (Aberration-Corrected Transmission Electron Microscopy, AC-TEM) je bila strukturna in kemična karakterizacija izvedena na atomskem nivoju, kar je dalo vpogled v razumevanje nukleacije in rasti. AC-TEM slikanje in spektroskopija energijske izgube elektronov sta pokazali, da so TiO nanokristali kamene soli občasno nastali v zgodnji fazi nukleacije po samo 20 ALD ciklusih. Razumevanje in nadzor nukleacije in rasti hibridnega nanomateriala sta ključnega pomena za doseganje novih lastnosti in večjo učinkovitost za široko paleto aplikacij, ki izkoriščajo sinergijske funkcije zloga.

Materiali z visoko električno in toplotno prevodnostjo, z mikrostrukturno stabilnostjo in visoko temperaturno trdnostjo so zelo privlačni za električno-elektronsko industrijo, pa tudi v posebni strojni industriji (aktivno hlajeni deli, raketne šobe, magnetna žica in kabli, konice varilnih elektrod). Pri temperaturah, ki so precej nad okolico, večina utrijevalnih mehanizmov, kot so trdne raztopine, hladna deformacija in izločevalno utrjevanje, postane neučinkoviti. Namreč, pri visokih temperaturah ratopljeni atomi v trdni raztopini utrjene kovinske zlitine ne morejo blokirati dislokacij, deformacijsko utrjene kovine se rekristalizirajo in postanejo zelo mehke, izločki v izločevalno utrjenih

Controlled synthesis of a hybrid nanomaterial based on titanium oxide and Single-Layer Graphene (SLG) using Atomic Layer Deposition (ALD), is also a known example in the design of the metallurgy process [15]. The morphology and crystallinity of the oxide layer on SLG can be tuned mainly with the deposition temperature, achieving either a uniform amorphous layer at 60°C or ~2 nm individual nanocrystals on the SLG at 200°C after only 20 ALD cycles (see Figure 2). The continuous and uniform amorphous layer formed on the SLG after 180 cycles at 60°C can be converted to a polycrystalline layer containing domains of anatase TiO₂ after a postdeposition annealing at 400°C under vacuum. Using Aberration-Corrected Transmission Electron Microscopy (AC-TEM), characterization of the structure and chemistry was performed on an atomic scale, and provided insight into understanding the nucleation and growth. AC-TEM imaging and electron energy loss spectroscopy revealed that rocksalt TiO nanocrystals were formed occasionally at the early stage of nucleation after only 20 ALD cycles. Understanding and controlling nucleation and growth of the hybrid nanomaterial are crucial to achieving novel properties and enhanced performance for a wide range of applications that exploit the synergetic functionalities of the ensemble.

Materials with a high electrical and thermal conductivity, respectively, with the microstructural stability and high temperature strength, are very attractive for the electric-electronic industry, and also in the special machine building industry (actively cooled parts, rocket nozzles, magnet wire and cables, welding electrode tips). At temperatures well above ambient, most of the strengthening mechanisms, such as solid-solution hardening, cold working and precipitation hardening, become ineffective. Namely, at high

zlitinah pa se ponovno raztopijo in se tako izgubi učinek utrjevanja. Možna rešitev za izboljšanje utrjevanja zlitin pri visoki temperaturi zato predstavlja utrjevanje z vlakni (izdelava kompozitov) in disperzijsko utrjanje. Izdelava kovinskih kompozitov temelji na uporabi ojačitvenih C-vlaken ali netopnih vlaken z visokim tališčem (Nb, W, ...). V industrijski praksi obstaja veliko znanih proizvodnih tehnologij za kompozit kovina-C, vendar noben od teh ne reši dveh težav: (i) vezave med matico in vlaknom, ki je izjemno šibka pri kompozitih kovina-C; (ii) doseganje visokega volumskega odstotka fino dispergiranih, nepovezanih grafitnih ali karbidnih delcev nano velikosti. Poleg tega je uporaba kompozita kovina-C pri visoki temperaturi omejena zaradi notranje oksidacije C-vlaken.

Vključitve majhnega odstotka dispergiranih, nepovezanih, finih disperzoidov nano velikosti v kovinsko matico je učinkovit način izboljšanja mehanskih lastnosti kovinskih materialov pri zelo visokih temperaturah. Pri takih disperzijsko utrjenih zlitinah dobimo učinek utrjanja z disperzijsko-dislokacijsko interakcijo, pri čemer disperzoidi ovirajo premike dislokacije. Dodatna zunanja napetost, ki je potrebna, da se dislokacija pri visoki temperaturi izogne nepovezanemu delcu in se lahko spet prosto giblje, je povezana z energijo za proces plezanja in energijo za naknadno ločitev dislokacijske črte od delca. Med fazo plezanja je potrebno zagotoviti dodatno energijo za dolžino nove dislokacije, ki se mora ustvariti. Hkrati del odseka dislokacije v stiku z delcem sprosti del svojega napetostnega polja (energija dislokacijske črte je nižja od polne energije v matici do sproščene energije na meji z delcem), tako da je potrebna dodatna sila za odstranitev dislokacije od delca. Skupni prag napetosti za premostitev dislokacije preko delca je največja vrednost

temperatures, solute atoms in solid-solution hardened metal alloys are not able to lock the dislocations, strain hardened metal recrystallizes and becomes very soft and precipitates in precipitation hardened alloys which go into the solution and their effect of hardening is lost. The possible solution for improved strengthening properties of alloys at high temperature therefore present the fibre strengthening (the composite formation) and dispersion strengthening. The metal-composite fabrication is based on the use of the reinforcement of C-fibre or non-soluble fibre with high melting (Nb, W,...). In the industrial praxis, there are many known production technologies for metal-C composite, but none of these solve the two problems: (i) The interfacial bonding matrix-fibre, which is extremely weak in metal-C composite; (ii) The attainment of a high volume percentage of finely dispersed, incoherent graphite or carbide particles of nano size. Furthermore, the use of metal-C composite at high temperature is limited because of the internal oxidation of C-fibre.

The inclusions of a small percentage of nanosized fine dispersed, incoherent, non-shearable dispersoids in a metal matrix is an efficient way of improving the mechanical properties of the metallic materials at very high temperatures. In such dispersion-strengthened alloys, the strengthening effect is obtained by dispersoids-dislocation interaction, whereby the dispersoids impede the dislocation motion. The additional supplied external stress, which is required so that the dislocation at high temperature avoids the incoherent particle and becomes again free to move, is associated with the energy for the climb process and the energy for subsequent detachment of the dislocation line from the particle. During the climbing stage, extra energy must be supplied for a new dislocation line length that has to be created. At the same time, the portion of the

dveh napetosti – napetosti za lokalno plezanje in napetosti za ločitev. Vendar pa je bilo navedeno, da je za nadzorovan premostitev oziroma odcepitev od delca potrebna le skromna sprostitev energije dislokacijske črte (okoli 6 %). Torej je očitno, da ima sprostitev energije dislokacijske črte pomembno vlogo, s katero delci zavirajo gibanje dislokacije. Takšna sprostitev poteka z difuzijskimi preuređitvami atomov na meji delec – matica. Obseg, v katerem dislokacija sprošča svojo energijo, je odvisna od časa plezanja in narave meje. Kot je bilo prikazano v literaturi [16], je lahko visoka stopnja dislokacijske relaksacije dosežena le pri šibko vezanih nepovezanih mejah z visoko specifično energijo. Zato bi morali potencialni kandidati za učinkovite disperzoide imeti kristalno strukturo, ki omogoča disperzoidom, da na meji z matico kažejo velike nepravilnosti v rešetki. Teoretično, če odstranimo disperzijske delce iz matice, dobimo matico, ki je okrepljena s "prazninami". Čeprav sprostitev energije dislokacijske črte poteka z difuzijskimi preuređitvami atomov na meji "delcev" – matic, s prazninami dobimo najvišjo stopnjo relaksacije energije dislokacijske črte in s tem največji učinek utrjanja. Glede na zgoraj navedeno je razvoj proizvodne tehnologije kovinskih materialov, ojačenih z mehurčki nano velikosti z visoko termodinamično in kemično stabilnostjo pri visokih temperaturah, ena od rešitev za visoko temperaturno utrjanje. Takšen material se izdela z notranjo oksidacijo nezveznega kompozita kovina-C s fino disperzijo C-delcev nano velikosti, kjer iz reakcije raztopljenega kisika z grafitom dobimo plinske produkte (CO in CO_2), ki se ne morejo vgraditi v kovinsko rešetko, in se prepletejo v prostoru, ki ga je predhodno zasedel grafit. Ti plinski produkti imajo večji specifični volumen kot trdni grafit, s čimer se vzpostavijo tlačne obremenitve v

dislocation line in contact with the particle relaxes part of its strain field (the line energy of dislocation is lower from the full energy in the matrix to the relaxed energy at the interface), such that an additional force is required to remove the dislocation from the particle. The overall threshold stress for dislocation bypass over the particle is the largest value of the two stresses - stress for local climb and for detachment. However, it was indicated that only a modest relaxation of the dislocation line energy (about 6 %) is necessary for detachment - controlled bypassing. So, it is obvious that relaxation of dislocation line energy plays an important role in the efficiency with which the particles inhibit dislocation motion. Such relaxation occurs by diffusional rearrangements of the atoms at the particle - matrix interface. The extent to which the dislocation relaxes its energy depends on the time of climbing and on the nature of the interface. As was shown in the literature [16], a high degree of dislocation relaxation can only be achieved at weakly bonded incoherent interfaces with a high specific energy. Therefore, the potential candidates for the effective dispersoids should have a crystal structure, which enables the dispersoids to exhibit a large lattice misfit at the interface with the matrix. Theoretically, if we remove the dispersion particles from the matrix, we would obtain the matrix strengthened with the "voids". While the relaxation of dislocation line energy occurs by diffusional rearrangements of the atoms at the "particle" - matrix interface, we obtain with the voids the highest degree of dislocation line energy relaxation and, hence, the greatest strengthening effect. According to the aforementioned, the development of the production technology of metallic materials strengthened with nanosized bubbles with high thermodynamically and chemically stability at high temperatures,

kovinski matici, kar posledično povzroča učinek utrjanja. Po drugi strani pa lahko takšno napetostno polje reagira z drsečo dislokacijo, s čimer se ovirajo premiki dislokacij.

4 Zaključki

Izdelava stabilnih funkcionalnih materialov na atomski ravni je končni cilj nanotehnologije in metalurgije. Različni procesi zahtevajo operacije ali uvedbo novih pristopov z visoko natančnostjo. Naša opažanja in pregled literature kažejo, da je postopek izdelave različnih materialov povezan z doseganjem finozrnate strukture. Zato je potrebno imeti globlje razumevanje glede kemijskih in fizikalnih procesov na nano ravni, s čemer se lahko izdelave materiale z najvišjo kakovostjo.

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represents one of the solutions of high temperature strengthening. Such a material will be produced with the internal oxidation of metal- C discontinuous composite with fine dispersion of nanosized C-particles, where the reaction of dissolved oxygen with graphite yielded the gas products (CO and CO_2), which cannot occur in the metal-lattice, and they are meshed in the space previously occupied by graphite. The gas products have a greater specific volume than solid graphite, thus establishing the compressive stresses in the metallic matrix and, consequently, causing the strengthening effect. On the other hand, such stress field can react with sliding dislocation, whereby they impede the dislocation motion.

4 Conclusions

Fabricating stable functional materials at the atomic scale is the ultimate goal of Nanotechnology and Metallurgy. In different processes, high-precision operations or approaches are needed. Our observations and literature review show that the process of manufacturing of various materials is related to achieving a fine grain structure on the nano level. Therefore, a deeper understanding is needed connected to the chemical and physical processes on the nano-level, which could be a guarantee for the highest quality materials.

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Viri in reference / References

- [1] Y.-C. Wang and S. Gunasekaran, "Spectroscopic and microscopic investigation of gold nanoparticle nucleation and growth mechanisms using gelatin as a stabilizer," *J. Nanoparticle Res.*, vol. 14, no. 10, pp. 1–11, Sep. 2012.
- [2] R. G. Palgrave and I. P. Parkin, "Aerosol Assisted Chemical Vapor Deposition of Gold and Nanocomposite Thin Films from Hydrogen Tetrachloroaurate(III)," *Chem. Mater.*, vol. 19, no. 19, pp. 4639–4647, Sep. 2007.
- [3] T. T. Kodas and M. J. Hampden-Smith, *Aerosol Processing of Materials*, 1 edition. New York: Wiley-VCH, 1998.
- [4] J. Kimling, M. Maier, B. Okenve, V. Kotaidis, H. Ballot, and A. Plech, "Turkevich Method for Gold Nanoparticle Synthesis Revisited," *J. Phys. Chem. B*, vol. 110, no. 32, pp. 15700–15707, Aug. 2006.
- [5] N. G. Bastús, J. Comenge, and V. Puntes, "Kinetically Controlled Seeded Growth Synthesis of Citrate-Stabilized Gold Nanoparticles of up to 200 nm: Size Focusing versus Ostwald Ripening," *Langmuir*, vol. 27, no. 17, pp. 11098–11105, Sep. 2011.
- [6] G. Schmid and B. Corain, "Nanoparticulated Gold: Syntheses, Structures, Electronics, and Reactivities," *Eur. J. Inorg. Chem.*, vol. 2003, no. 17, pp. 3081–3098, 2003.
- [7] S. V. Kolpakov, V. A. Parshin, and A. N. Chekhovoi, "Nanotechnology in the Metallurgy of Steel", *Steel in Translation*, 2007, Vol. 37, No. 8, pp. 716–721, doi: 10.3103/S0967091207080177.
- [8] Chekhovoi, A.N., *Synergetics of Nanostructuring: Nanotechnology for Manufacturing: Appendix to the Journal Spravochnik*, Moscow: Mashinostroenie, 2006, no. 9, p. 24.
- [9] Baranov, S.M., Bezirozvannykh, A.V., and Chekhovoi, A.N., Influence of an Active Impurity on the Mechanical Strength and Few-Cycle Fatigue of High Strength Steel, *Dokl. Akad. Nauk*, 1981, vol. 261, no. 4, pp. 856–860.
- [10] Yu. A. Minaev, "Thermochemical Nanotechnology in Metallurgy and Machine Building", *Metallurgist*, Vol. 55, Nos. 11–12, March, 2012.
- [11] Yu. A. Minaev, "Functional steel alloys hardness and wear improving on a basis of phenomena of grain boundary phase transition" *Adv. Mat. Research*, 189–193, 4438–4441 (2011).
- [12] M. Yahaya et al., "Microstructures and Mechanical Properties of Ti-Nb Alloy at Different Composition of Nb Produced via Powder Metallurgy Route", *Materials Science Forum*, Vol. 863, pp. 14-18, 2016.
- [13] V.A.Andreyachshenko,A.B.Naizabekov, Microstructural and mechanical characteristics of AlSiMnFe alloy processed by equal channel angular pressing, *Metalurgija*, Vol.55 No.3 July 2016.
- [14] Aiyuan M., Xuemei Z., Shixing W., Jinhui P., Study on dechlorination kinetics from zinc oxide dust by clean metallurgy technology, 2016, <https://doi.org/10.1515/gps-2015-0041>.
- [15] Yucheng Z., Carlos G.-N., Ivo U.‡, Michler J., Agrawal P., Rossell M.D., and Rolf E., Atomic Layer Deposition of Titanium Oxide on Single-Layer Graphene: An Atomic-Scale Study toward Understanding Nucleation and Growth, *Chem. Mater.*, 2017, 29 (5), pp 2232–2238.
- [16] J. Rösler, E. Arzt: A new model-based creep equation for dispersion strengthened materials; *Acta metall.*, Vol. 38, No. 4, 671-683, 1990.