

INNOVATIVE METHOD TOWARD MAKE STEADY NANOCRYSTALLITES BY SEVERE FORCED DEFORMATION

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Abstract

A new method to produce bulk nanocrystalline metal-matrix composites is presented. A metal powder is treated to obtain a relatively brittle layer with a defined thickness on the surface. The precompact powder is deformed by High-Pressure Torsion until a dense bulk nanocrystalline material is formed. Due to fragmentation of the thin layer, it is possible to incorporate nanometer sized dispersions into the nanocrystalline metal-matrix. As example an oxidized nickel powder is investigated where thermal stability and microhardness are extraordinarily enhanced.

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1.Introduction

High Pressure Torsion, Nano composite Nanocrystalline materials have been a subject of extensive research over the past decades due to the effect of the nanocrystalline state on the microstructure and the mechanical, thermophysical, optical and magnetic properties of metals and alloys . Development of novel methods for large-scale processing of nanostructured materials is a challenging task. Methods of severe plastic deformation are well known procedures to obtain dense ultra fine grained or even nanocrystalline bulk materials with unique properties, which cannot be obtained by nanostructured materials produced by other techniques .

A large number of different severe plastic deformation methods were developed in recent years . One of these severe plastic deformation methods is High-Pressure Torsion , where the deformation is obtained mainly by simple shear. High pressure torsion is a simple technique to apply very large strains in a material due to the applied hydrostatic pressure during the deformation. It is ideal to investigate the limits in refinement which one can obtain in a material at a certain deformation temperature and strain rate .

The evolution of the microstructure of single phase materials deformed by High pressure torsion shows a relatively uniform behaviour: With increasing strain the size of the structural elements continuously decreases until -at strains larger than a critical value - no further microstructural refinement can be observed. This general phenomenon in High pressure torsion is independent of the material and the processing parameters and has been observed in many pure metals and alloys. Only the minimum size of the crystallites in the saturation and the necessary strain to reach this so called steady-state region are affected. The most important parameters influencing the refinement of the microstructure and the necessary strain to reach the onset point of saturation in single phase materials are the deformation temperature, alloying, the strain rate and the mode of deformation . In bulk microcrystalline nickel, a typical saturation microstructure with a mean grain size of ~200 nm after High pressure torsion deformation at room temperature can be obtained . It is impossible to further decrease grain size by processing the samples to higher strains once the saturation region is reached. This limitation becomes even more clearly visible if High pressure torsion is applied to electrodeposited nanocrystalline nickel. Remarkable grain coarsening is induced during the High pressure torsion deformation and the material is transformed from the nanocrystalline microstructure into an ultrafine grained microstructure .

Nevertheless the saturation size of the structural elements can be decreased distinctly with decreasing deformation temperature. High pressure torque deformation of MC bulk nickel at -196°C leads to a saturation microstructure with a mean grain size of approximately 100 nm . Unfortunately, the microstructure of severe plastic deformation pure metals in the as-deformed state is thermally unstable and annealing at low temperatures leads to recrystallization and coarsening of the microstructure, which in turn alters material properties. one major goal for material development must be the enhancement of the thermal stability of the produced micro structure to make it suitable for technical applications. Because the limit in the structural refinement during severe plastic deformation cannot be overcome with severe plastic deformation of bulk single phase materials, we used a new processing route to circumvent these limitations. Nickel powders were consolidated via High pressure torsion to incorporate fine dispersed nickel oxide particles in the nickel matrix which were found to influence the obtainable saturation microstructure, mechanical properties and furthermore the thermal stability of the structure.

1.1 processing of the materials

The High pressure torsion equipment used for processing the materials present in this paper is described in detail in. Two states of nickel powder were used in this study: (i) as-received nickel powder (99.8%, 70-100 microns and (ii) as-received nickel powder (99.9%, 3-7 microns which was also additionally annealed before compaction. The powders were first precompacted in the High pressure torsion tool and subsequently deformed by High pressure torsion at room temperature. Both precompaction and the High pressure torsion deformation were carried out in air. The precompacted samples with a diameter of 8-14 mm and a thickness t of ~ 0.8 mm were deformed to different equivalent strains until the steady state, where no further refinement of the microstructure takes place. The pressure during deformation was varied between 2.5-6 GPa and the rotation speed was kept constant at 0.2 rpm. After deformation, the deformed samples were additionally heat treated for 1 h at three different temperatures (243°C , 418°C and 591°C) corresponding to 0.3, 0.4 and 0.5 times of the melting temperature to investigate the thermal stability.

For comparison, experiments on microcrystalline bulk nickel were also performed. Microstructures were characterized in a scanning electron microscope type LEO 1525 using back scattered electrons and in a transmission electron microscope. All microstructural investigations were performed at a distance of 1 mm from the High pressure torsion disc edge in all samples. Grain size distribution was measured using TEM bright-field images. Vickers microhardness measurements were performed on a BUEHLER Mircomet 5100 using a load of 1000 g. XRD measurements for phase analysis were performed with a Seifert 3000 PTS- X-ray diffraction system. At first the behaviour during High pressure torsion deformation of nickel powders with a particle size of approximately 70-100 microns and nickel powder with a particle size of 3-7 microns in the as received condition is considered. Due to the large surface area especially in the latter case, a high amount of naturally formed oxide is introduced in the later bulk compacts. The powders were firstly precompacted directly in the High pressure torsion tool and subsequently High pressure torsion deformed. During the High pressure torsion deformation the powders are consolidated, the naturally formed oxides get fragmented and homogenously distributed and simultaneously the grain size is refined. The process of continuous subdivision of the initial grain structure in bulk metals is well documented in literature . In contrast to bulk metals, larger strains must be applied for the High pressure torsion consolidation of powders to reach the saturation region. All here presented samples were High pressure torsion deformed until the saturation region was reached, in which no further refinement of the microstructure takes place. Grain sizes between 100-150 nm were estimated from the back scattered electrons micrographs. However, also some grains with a size below 50 nm were observable. Nevertheless, no considerable influence of the different particle sizes of the nickel powders before deformation on the final microstructure was found. These first experiments revealed that the fraction of naturally formed surface oxides in the as received powder is apparently too low to exhibit a distinct influence on the final microstructure. To increase the fraction of oxides, the initial powder was additionally annealed at 400°C for 10 minutes in air to obtain a thin oxide layer of on the surface of the particles . Figure C1 displays a schematic illustration of the nickel powder particles and the thin oxide layers on the surface of the particles after the annealing treatment.

1.2 Process

Afterwards, the oxidized nickel powder was again precompacted and subsequently High pressure torsion deformed until the saturation region was reached. BSE micrographs of the samples after High pressure torsion revealed a smaller saturation grain size compared to the non-oxidized nickel powder sample, which is clearly below 100 nm. During the deformation, the nickel powder particles are heavily deformed and elongated whereas the grain size is refined at the same time (a schematic sketch of the process is shown in Figure C1)

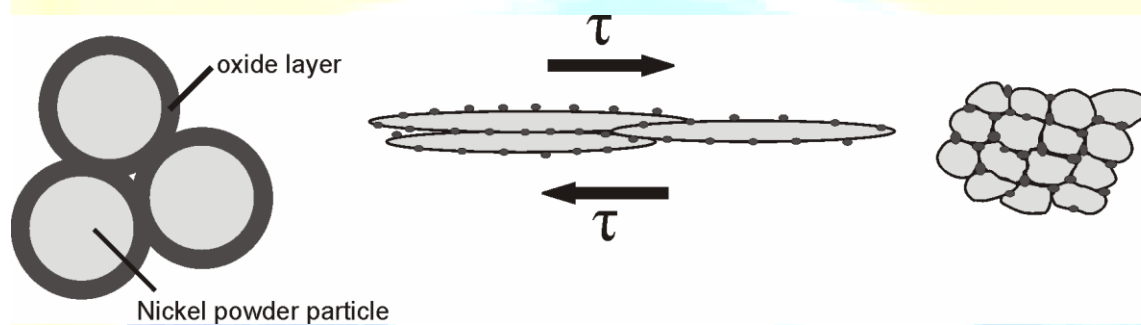


Figure C1: (a) Nickel oxide layers on nickel particles before deformation, (b) the fracture of these layers during deformation and (c) the assumed distribution of the nickel oxide particles in the nickel matrix after deformation.

2. Experimental Analysis

The nickel oxide layers on the surface of the particles fracture during the deformation into small particles. Increase in deformation finally leads to a nanocrystalline nickel matrix with dispersed nickel oxide particles. At the moment, the distribution of the nickel oxide particles in the nickel matrix is not completely clear. Due to the nanometer size of the nickel grains we would rather expect the oxide particles to be dispersed along the grain boundaries and triple junctions of the grains. This assumption was further confirmed by transmission electron microscope images, where no particles were visible inside the grains. The nickel oxide particles also have an influence on the structural evolution and final attainable microstructure of the samples: They should pin dislocations and

grain boundaries, therefore deterring recovery and recrystallization during the deformation and therefore a finer microstructure is obtained.

Microhardness was measured from the center to the edge of the different High pressure torsion deformed samples (i.e. increasing applied strain). The results of the evolution of hardness as a function of the applied equivalent strain is plotted in Figure C2. All graphs show a similar trend: small hardness values at low equivalent strains, which increase with increasing applied equivalent strain and a saturation of hardness at large deformations which corresponds to the saturation in the grain size refinement.

However, there exist distinct differences between the samples. The High pressure torsion induced grain size reduction in the beginning of the deformation leads to a strong hardening of the HPT deformed bulk nickel. The hardness increases from 0.6 GPa of the undeformed nickel sample up to a hardness of 2.8 GPa in the saturation region, which is reached at applied equivalent strains of about 20. Processing the sample to higher equivalent strains is not leading to a further increase in hardness as already mentioned. The same behaviour can be seen for the bulk nickel sample which was High pressure torsion deformed at -196°C . Nevertheless, the hardness in the saturation region is higher and reaches values of approximately 4.4 GPa. In this case, the increase in hardness results primarily from the reduction in grain size. The High pressure torsion bulk nickel sample deformed at room temperature exhibits a mean grain size of 200 nm, whereas the sample deformed at -196°C shows a mean grain size of approximately 100 nm. The evolution of hardness of the High pressure torsion consolidated samples of nickel powder is similar, but the necessary strain to reach saturation in hardness is much higher compared to High pressure torsion deformed bulk nickel. On the other hand, one should note that the obtainable hardness (5 GPa) of the High pressure torsion nickel powder samples is 1.7 times higher compared to that of High pressure torsion bulk nickel. The samples of the High pressure torsion consolidated oxidized nickel powder reach the highest hardness values (6.8 GPa) after an applied strain of about 250. The hardness is more than 10 times or 2.5 times higher compared to MC nickel or MC High pressure torsion deformed bulk nickel, respectively. The high hardness of these samples is primarily attributed to strengthening from further grain size refinement and maybe to the nickel oxide particles.

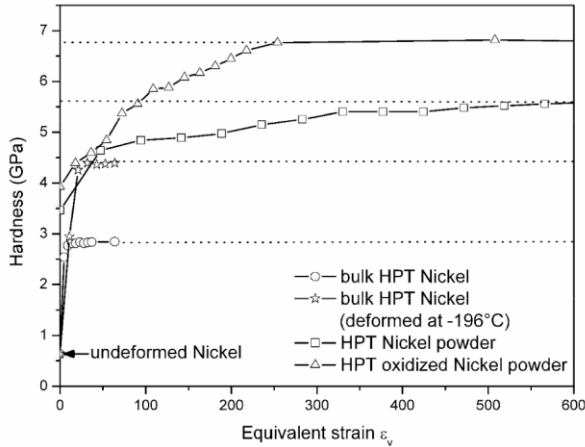


Figure C2: Microhardness of High pressure torsion bulk nickel deformed at room temperature and at -196°C and of High pressure torsion consolidated samples of nickel powder and oxidized nickel powder as a function of the applied equivalent strain. The hardness of bulk nickel without any deformation is 0.64 GPa (indicated by an arrow). Transmission electron microscopy was used to investigate the microstructure of the High pressure torsion consolidated sample of oxidized nickel powder in more detail. The TEM sample was cut at a distance of 1 mm from the edge of the High pressure torsion disk. Figure C3 shows a bright field image of the microstructure of the sample after High pressure torsion, with insets showing the corresponding selected area electron diffraction pattern and the grain size distribution. The bright field image reveals a nanocrystalline structure with few larger but as well very small grains, where the different grains can hardly be distinguished from each other. The grains have a rather broad grain size distribution making the estimation of the grain size difficult.

The grain size distribution was measured using several TEM images. Most of the grains have a size between 10-30 nm, but there is also a considerable amount of grains with a size somewhat below 10 nm as well as few larger grains with grain sizes of ~ 30 to 100 nm. The mean size is 29.8 nm with a standard deviation of 20.6 nm. Furthermore, nickel oxide particles cannot be distinguished from nickel matrix grains.

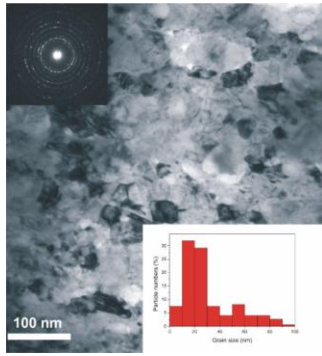


Figure C3: The bright-field transmission electron micrograph shows the microstructure of the High pressure torsion consolidated sample of oxidized nickel powder. The corresponding pattern and the grain size distribution are shown as insets. The number fraction of grains vs. grain size of the High pressure torsion consolidated sample of oxidized nickel powder was measured by TEM bright field images. In addition, the High pressure torsion consolidated samples of nickel powder and oxidized nickel powder were investigated by X-ray diffraction in order to determine the phases present. The High pressure torsion consolidated sample of nickel powder exhibits only nickel peaks in the pattern. No other phases were detected. In contrast, the formation of an additional phase, namely nickel oxide, is clearly visible in the XRD pattern of the High pressure torsion consolidated sample of oxidized nickel.

In general, pure materials processed by severe plastic deformation are thermally unstable due to the huge stored energy in form of crystalline defects like dislocations and “non-equilibrium” grain boundaries in the as-deformed state. A way to stabilize the fine, as-deformed microstructure is the presence of a high density of smallest uniformly distributed second phase particles. To study the thermal stability, the as-deformed High pressure torsion consolidated powder samples were annealed at three different temperatures for 1 h and changes in microhardness were subsequently measured (Figure C4). The High pressure torsion consolidated sample of nickel powder displays three distinguishable stages during the annealing treatment: the sample has an initial hardness of about 5 GPa, which stays nearly constant until 0.3 T_m (T_m being the melting temperature). The hardness rapidly drops at higher annealing temperatures between 0.3 – 0.4 melting temperature which might be due to grain growth. Further grain growth occurs at higher annealing temperatures leading to a further slight decrease in hardness reaching values of 1.7 GPa at 0.6 T_m. Microstructural observations by scanning electron microscopy

confirmed these findings. The High pressure torsion consolidated sample of oxidized nickel powder shows higher initial hardness values of about 6.8 GPa which slowly decrease with higher annealing temperatures up to 0.4 T_m. In this temperature range recovery may take place, which is not affecting the grain size considerably as approved by scanning electron microscopy. At higher annealing temperatures (0.5 T_m) the hardness decreases somewhat faster reaching values still in the range of the initial hardness of the High pressure torsion consolidated sample of nickel powder before the annealing treatment (4.8 GPa) or even larger than the hardness of the at -196°C High pressure torsion deformed bulk nickel. Marginal grain growth set in leading to an estimated grain size of approximately 100 nm. It is obvious that the fine dispersed oxides in the nickel matrix have a remarkable effect on the thermal stability: The High pressure torsion oxidized nickel powder samples exhibit an extended recovery stage, therefore the onset temperature for grain growth is increased and the structure remains nanocrystalline even at high annealing temperatures of 0.5 T_m with high hardness values of about 4.8 GPa. The fine microstructure is stabilized by the oxide particles because grain growth is impeded by uniform distributed particles due to their influence on dislocation motion and pinning of grain boundaries. The thermal stability is clearly improved compared to other results reported in literature on the thermal stability of High pressure torsion deformed MC bulk nickel considering also different purity and annealing treatment and compared to the High pressure torsion bulk nickel samples deformed at -196°C where low annealing temperatures resulted in recrystallization and grain growth as well.

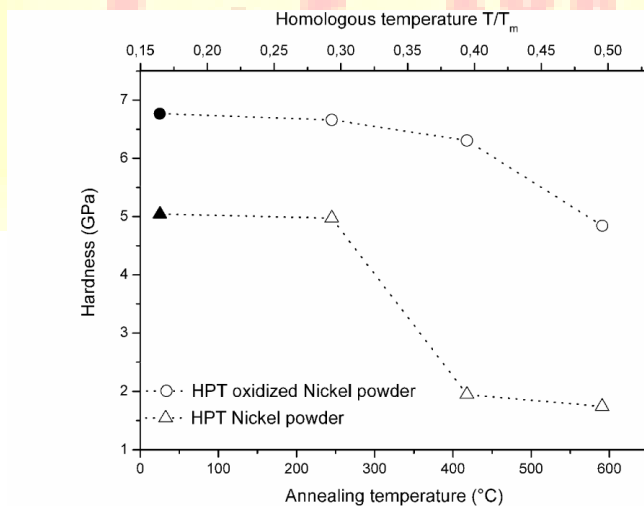


Figure C4: Evolution of the microhardness of the High pressure torsion consolidated samples of nickel powder and oxidized nickel powder as a function of the annealing temperature. The hardness of the as-deformed samples is also included (filled symbols). To prove possible application of the process to other materials, experiments with oxidized aluminium powders were performed. The results showed that the method can be successfully applied to other powders as well. Oxidation of the initial metal powders is the easiest way to produce a metal matrix composite of type MO_x , whereby M and O stay for the metal and corresponding oxide, respectively. Another possible application might emerge from the initial carburization of metal particles to obtain metal matrix composites of type MC_x (C stays for carbon). By the use of coating processes almost arbitrary combinations of thin coatings and substrate metal might be achieved giving the opportunity to produce completely new types of metal matrix composites of type $M_1M_2X_y$ (X stays for the nonmetallic component).

3. Conclusion

The new processing route proposed in this study offers an easy way to produce bulk nanocrystalline metal matrix composites with nanometer sized oxide dispersions without any complicated steps during the processing. Initial micrometer sized powders are oxidized via a simple annealing treatment and subsequently High pressure torsion consolidated until a fully dense bulk material is obtained. The oxidation of the initial powders has a huge impact on the final microstructure as well as on the mechanical properties and the thermal stability of the consolidated material. A truly nanocrystalline metal matrix is produced which is stabilized with homogeneously distributed nanometer sized oxide particles. The second phase particles strengthen the matrix effectively and an excellent structural stability is reached due to the pinning effect of the oxide particles. Additional advantages of the process are the use of micrometer sized powders instead of nanometer sized powders which are easier to handle and to produce as well as the avoidance of particle cluster formation during processing which are drawbacks in conventional powder consolidation techniques. The combination of a simple processing route, the possible application on arbitrary material combinations and the potential up-scaling of the process makes it an attractive candidate for further industrial application.

4.References

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