Final report

Microstructure and mechanical properties of advanced materials processed by powder metallurgy

Péter Jenei

During my research I examine materials processed by powder metallurgy methods. I have used several advanced procedure such as Spark Plasma Sintering (SPS), Freeze Casting, and High Pressure Torsion (HPT). In the following I will summarize the results. The chapters are arranged according to the research plan. In each chapter (where relevant) I mention my ongoing research on the topic

1. Spark Plasma Sintering

1.1. The influence of carbon nanotube addition on the phase composition , microstructure and mechanical properties of 316L stainless steel [1]

An investigation was conducted to study the effect of CNT addition on the microstructure and the mechanical behavior of 316L steel. Samples with 0, 1 and 3 wt.% of CNTs were sintered by SPS method. The following conclusions were drawn from the experiments:

A) The major phase for all samples was a γ-austenite with the fractions between 0.68 and 0.81. In the sintered CNT-free sample, beside the γ-austenite considerable amounts of bcc α-phase and Fe_3O_4 phase were detected. During sintering at high temperature, the fraction of the α-phase developed during powder milling decreased due to a reverse martensitic transformation. The Fe_3O_4 phase was also formed during the sintering process. The addition of CNTs resulted in the development of an Fe_3C phase. The fraction of this phase increased with increasing the CNT content.

B) Sintering of the 316L powder led to a decrease in the dislocation density and a concomitant increase in the crystallite size due to the recovery and recrystallization of the severely milled microstructure. The addition of CNTs impedes these processes, therefore the dislocation density and the grain size in the 316L-CNT composites were higher and smaller, respectively, than in the CNT-free material. The increase of the CNT content from 1 to 3% did not yield a smaller grain size or a higher dislocation density. Most probably, the clustering of the CNTs in the 316L-3CNT sample decreased the hindering effect of a unit amount of CNTs on recovery and recrystallization.

C) The CNT addition increased the hardness of the sintered 316L alloy due to the hardening effect of the CNTs, the Fe_3C phase, the smaller grain size and the higher dislocation density. At the same time, clustering of CNTs yielded a weaker bonding between the 316L grains, therefore 3% CNT addition resulted in a significant decrease in the bending strength.

1.2. The influence of BN additives on the phase composition, microstructure and mechanical properties of 316L steel [2]

The effect of BN addition on the microstructure and the mechanical properties of commercial 316L stainless steel was studied. Samples containing 0, 0.5 and 2 wt.% BN were produced using high energy milling and SPS method. The following results were obtained:

A) A high fraction (27-28 %) of α'-phase formed beside the major γ-phase phase during the milling process. During sintering at high temperature, the fraction of the α'-phase decreased due to a reverse martensitic phase transformation. It seems that the BN additive promotes this transformation since the fraction of α'-phase is considerably lower in the composites. Fe_3O_4 and $Cr_{23}C_6$ phases were also formed during the consolidation process.

B) All samples show inhomogeneous grain structure. Large particles can be seen in the fine grained matrix. The larger particles are fragmented into smaller grains. The addition of 0.5% BN decreased the grain size in both regions, but further BN addition did not result in a finer grain structure. The microhardness of the fine grained part was higher (irrespectively of the BN content) duo to the much lower grain size.

C) The addition of 0.5% BN did not result in a significant change in the dislocation density. The increase of the BN content from 0.5 to 2% yielded a higher dislocation density due to the hindering effect of BN particles on the annihilation of dislocations during sintering. The microhardness, the bending strength and the elastic modulus slightly decreased with increasing the BN content. This effect can be attributed mainly to the lower α'-phase fraction and the weak bonding between the 316L and the BN grains.

1.3. Continue of the research

We prepared ODS steels with Y_2O_3, Al_2O_3 disperse phases. Commercial austenitic and martensitic powders were used for sample preparation. An efficient dispersion of nano-oxides in ODS steels was achieved by attritor milling. The milling process was performed also wet (in ethanol) and dry condition. The powder was consolidated by SPS method. In this work we study the high-temperature creep properties of the materials.

In order to investigate the creep of ODS steel samples we have improved a high-temperature indentation creep device at my department. The creep of the very hard ODS steels can only be studied at high temperatures (600-900 °C), where considerable oxidation may occur. This has a significant effect on deformation, therefore the creep device should work in order to use it under inert gas (e.g. argon) atmosphere. From these measurements the activation energy and the strain rate sensitivity parameter can be obtained, as well as the deformation mechanisms can be deduced from the differences between the lattice defect structures observed before and after creep test. The results are under evaluation and publication.

2. Freeze casting

2.1. Cu–Ni Alloy Foams via Freeze Casting [3]

Porous metals have attracted great attention for their functional and structural applications; however, they often possess limited applicability in their pure form for the areas requiring decent strength and corrosion resistance. In this research, pure copper (Cu), pure nickel (Ni), and Cu–Ni alloy foams with five different compositions are successfully fabricated using freeze casting, resulting in open-pore structures with varied porosity (from 55% to 75%). Their varied morphologies and crystal sizes are compared, and the lattice parameters and crystal sizes are calculated. The corrosion resistance of the synthesized Cu–Ni alloy foams was superior to those of the pure Cu and Ni foams. For example, the weight loss rate of the Cu_7Ni_3 alloy foam was six times and five times slower than those of the pure Ni and pure Cu foams in a sulfuric corrosive environment, respectively. The yield strength of Cu_7Ni_3 alloy foam (53 ± 2% porosity) was 72 ± 2 MPa and its yield strength, when normalized by the Gibson-Ashby model, was the largest with a value of up to 852 ± 3MPa. The elastic modulus and hardness values of the Cu–Ni alloy foams were varied in the range of 73.4–152.4 GPa and 1.6–4.7 GPa, respectively. The strategic processing insights obtained in this project can also apply to other alloy foams that can form partial or complete solid solutions.

2.2. Compressive behavior of Cu-Ni alloy foams: Effects of grain size, porosity, pore directionality, and chemical composition [4]

Cu-Ni foams compression behavior was studied parallel and perpendicular to the freezing direction up to an engineering strain of 0.4. The following conclusions can be drawn from the results:

A) For compression parallel to the freezing direction, the Cu-Ni foams behaved in accordance with the compression model, except for the pure Ni foam. Ni foam had a very low relative density (~ 0.25), thus the very thin struts may have buckled under the vertical load. Therefore, the Gibson-Ashby (GA) model is more appropriate for the calculation of yield strength and the elastic modulus for the compression of Ni foam parallel to the freezing direction. The yield strength of the struts was higher for the alloys than for the pure metal foams.

B) In the classical compression model, the constants (C_{E}^{C} and C_{σ}^{C}) which are used for the calculation of the elastic modulus and yield strength, have the same value. Our calculations revealed that variation in the thickness of the struts resulted in a C_{E}^{C} that was significantly smaller thanC_{σ}^{C}. This difference was also observed experimentally for the studied Cu-Ni foams.

C) The behavior of the Cu-Ni foam perpendicular to the freezing direction was successfully described by the GA model, and the theoretical calculations also supported the trend that the measured elastic modulus decreased with increasing variation in strut thickness. Therefore, the C_{E}^{GA} constant, which was used to calculate elastic moduli, was smaller than the value obtained for the classical GA model.

D) The absorbed energy measured during compression up to a strain of 0.4 was higher for the alloys than for the pure foams, irrespective of the direction of compression. Therefore, we

conclude that alloying improves the compression performance of Cu and Ni foams processed using freeze casting.

2.3. Continue of the research

Lithium-ion batteries are used in a wide range of applications such as mobile phones, electronic devices and automobiles; however, they have not fully satisfied the issues raised by the low theoretical capacity of graphite anode for the current market demanding high capacity and high output. Therefore, the recent development of anode materials has been actively pursued to replace the carbonaceous anode materials. In particular, transition metal oxides (MO, where M is Co, Ni, Fe, Cu, etc.) among various high-capacity anode materials are attracting significant attention as a potential high-capacity anode material with high theoretical capacity ranging from 500 $mAhg^{-1}$ to 1000 $mAhg^{-1}$. Among them, nickel oxide (NiO) has a considerable theoretical capacity of 718 $mAhg^{-1}$, but its conductivity is rather poor, lowering the charging and discharging time. Using of porous and nanostructured electrodes could partially solve about high specific surface which increase the contact of active material, short Li diffusion path and superior accommodation of the strains of Li insertion/extraction. In our current research, Ni foam was fabricated via a freeze-casting method and porous NiO/Ni anode system was then created through a simple thermal oxidation. The microstructure of the fabricated porous NiO/Ni anode system was analyzed using FE-SEM, EDS and XRD. Additionally, its battery performance was evaluated using a standard half coin-cell test.

3. Metallic powders consolidated by High Pressure Torsion [5]

Coarse-grained aluminum powder with 99.5 wt% purity was consolidated by high-pressure torsion (HPT) technique at room temperature using a low carbon steel powder holder. In this process, the powder experiences a semi-constrained condition because the internal wall of the powder holder can expand under the load applied during HPT. The microstructure was characterized by electron backscatter diffraction and X-ray line profile analysis. The numbers of HPT turns were 1, 2 and 4. The following results were obtained:

A) A high relative density was achieved already after 1 turn of HPT which slightly increased with increasing number of revolutions and reached 99.83% after 4 turns. The size of the particles in the initial powder was between 5 and 40 μm. In the HPT-processed samples, the grain size decreased with increasing both the distance from the disk center and the number of turns. However, between 2 and 4 turns further grain refinement was not observed. The smallest grain size with the value of 0.41 μm was achieved at the periphery of the disks processed for 2 and 4 turns. The fraction of HAGBs increases with increasing the distance from the disk center, however consider- able difference between the HAGB fractions determined at the half- radius and the periphery was not observed. The highest fraction of HAGBs was achieved at the periphery of the disk processed by 4 revolutions (~73%).

B) The dislocation density increased with increasing both the distance from the disk center and the number of HPT turns. The dislocation density is a monotonously increasing function of the

shear strain applied in HPT processing. The maximum dislocation density was 6.8×10^14 m^−2 which was achieved at the periphery of the sample processed by 4 turns.

C) The hardness increases with increasing both the number of turns and the distance from the center even after 4 turns. The maximum hardness value measured at the periphery of the disks processed by 4 turns was about 135 HV. Two-dimensional hardness maps measured on the cross-section of the disks revealed a hardness inhomogeneity in the axial direction.

D) The yield strength at the half-radius of the disks obtained by tension increased with increasing number of turns and achieved a maximum value of ~195 MPa. The yield strength versus grain size relationship obeys the Hall-Petch equation with a similar slope as determined for bulk UFG Al1050 with a similar impurity content. At the same time, the friction stress for the consolidated Al was higher than that for the bulk counterpart, most probably due to the oxide/hydroxide phase formed from the native layer on the powder particle surfaces. The sample consolidated by 4 turns of HPT exhibited a high ultimate tensile strength of ~373 MPa and a large elongation to failure of ~22%. The good tensile ductility is most probably caused by the enhanced strain hardening ability and the low porosity of the samples.

4. Nanoparticles prepared by sonoelectrodeposition

4.1. Structure and Magnetic Properties of Nanocrystalline $Fe_{55}Pd_{45}$ [6]

$Fe_{55}Pd_{45}$ nanoparticles were prepared from iron acetate and palladium acetate by sonoelectrodeposition. The as-prepared nanoparticles were annealed at various temperatures from 450 °C to 700 °C for 1 h in order to study the effect of heat treatment on the phase composition, particle size and magnetic properties. The phase composition and the crystallite size of the annealed samples were determined by X-ray diffraction while the particle size was studied by transmission electron microscopy.

The crystallite size of $Fe_{55}Pd_{45}$ nanoparticles was about 8 nm. After annealing at various temperatures, the samples showed hard magnetic properties with the maximum room-temperature coercivity of about 1.1 kOe. The coercivity of the samples was strongly influenced by the crystalline phase composition. It was found that the as-prepared sample was a single phase disordered fcc Pd(Fe). With increasing temperature, ordered $L1_0$ FePd and bcc Fe phases were formed. The highest degree of ordering was achieved at 550 C which yielded a significant increase in the room-temperature coercivity from 0.5 kOe to 1.1 kOe. Further increase in the annealing temperature led to a reduction of coercivity, in accordance with the formation of a disordered fcc gamma-FePd. Beside the phase transformation, significant coarsening of the particles was also observed during annealing. The average crystallite size grew from about 8 nm to 50– 70 nm. This study demonstrates the strong temperature dependence of the structure and magnetic properties of $Fe_{55}Pd_{45}$ nanoparticles prepared by sonoelectrodeposition.

4.2. Continue of the research

Three addition Fe_xPd_{100-x} (x = 0.5, 0.6 and 0.63) nanoparticles were prepared beside nanocrystalline $Fe_{55}Pd_{45}$ powder. The nanoparticles were annealed at various temperatures from

450 °C to 700 °C for 1 h. In our current research the phase composition and the coercivity of the as-received and the annealed samples was examined. We are studying the relationship between phase composition and coercivity.

References

[1] P. Jenei, C. Balázsi, Á. Horváth, K. Balázsi, J. Gubicza, The influence of carbon nanotube addition on the phase composition , microstructure and mechanical properties of 316L stainless steel consolidated by spark plasma sintering, J. Mater. Res. Technol. 8 (2018) 1141–1149. doi:10.1016/j.jmrt.2018.07.019.

[2] P. Jenei, C. Balázsi, Á. Horváth, K. Balázsi, J. Gubicza, The influence of BN additives on the phase composition , microstructure and mechanical properties of 316L steel consolidated by spark plasma sintering The influence of BN additives on the phase composition , microstructure and mechanical properties of 316, IOP Conf. Ser. Mater. Sci. Eng. 426 (2018) 012020. doi:10.1088/1757-899X/426/1/012020.

[3] K. Nam, S. Lee, K. Hong, J.S. Kang, H. Jo, H. Park, et al., Freeze Casting is a Facile Method to Create Solid Solution Alloy Foams: Cu-Ni Alloy Foams via Freeze Casting, Adv. Eng. Mater. 1801265 (2019) 1801265. doi:10.1002/adem.201801265.

[4] J. Gubicza, P. Jenei, K. Nam, C. Kádár, H. Jo, H. Choe, Compressive behavior of Cu-Ni alloy foams: Effects of grain size, porosity, pore directionality, and chemical composition, Mater. Sci. Eng. A. 725 (2018) 160–170. doi:10.1016/j.msea.2018.04.018.

[5] M. Khajouei-Nezhad, M.H. Paydar, R. Ebrahimi, P. Jenei, P. Nagy, J. Gubicza, Microstructure and mechanical properties of ultrafine-grained aluminum consolidated by high-pressure torsion, Mater. Sci. Eng. A. 682 (2017) 501–508. doi:10.1016/j.msea.2016.11.076.

[6] N.H. Luong, T.T. Trung, T.P. Loan, N.H. Nam, P. Jenei, J.L. Lábár, et al., Structure and Magnetic Properties of Nanocrystalline Fe55Pd45 Processed by Sonoelectrodeposition, J. Electron. Mater. 46 (2017) 3720–3725. doi:10.1007/s11664-016-5269-8.