**Microstructure of ball milled and compacted Co-Ni-Al alloys from β range**

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| Keywords:      | Co-Ni-Al alloys, powder metallurgy, hot compacting, TEM, STEM-HAADF                         |
Microstructure of ball milled and compacted Co-Ni-Al alloys from β range

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Keywords. Co-Ni-Al alloys, powder metallurgy, hot compacting, TEM, STEM-HAADF.

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Summary

Two alloys in the β phase of compositions Co\textsubscript{28.5}Ni\textsubscript{36.5}Al\textsubscript{35} and Co\textsubscript{35}Ni\textsubscript{30}Al\textsubscript{35} were ball milled as powders in a high energy ball mill for 80 hours. The formation of amorphous structure was observed already after 40 hours of milling and further milling did not change their structure. Analytical and high resolution transmission electron microscopy (TEM, HREM) examination of powder’s structure showed that within the amorphous matrix the nanoparticles of L1\textsubscript{0} phase of size of about 5 nm were observed. The hot pressing in vacuum of milled powders under the pressure of 400 MPa at 700°C for 12 min resulted in formation of compacts with density of about 70% of the theoretical one. The additional heat treatment at 1300°C for 6 hours followed by water quenching, lead to significant improvement of density and promoted martensitic transformation detected by a broad heat effect. The characteristic temperatures of this transformation were determined by DSC measurements and only small differences within examined alloys compositions were observed. TEM structure studies of heat treated alloys were performed on samples prepared by Focused Ion Beam (FIB) method. The structure was composed of grains of size of about 500 nm of an ordered β (B2) phase. Additionally some grains were identified as the ordered γ phase (γ’). The chemical composition of heat treated
alloys was determined by energy dispersive spectroscopy (EDS) technique, applying the high angle annular dark field (HAADF) detector. It allowed to detect a significant amount of oxides within alloys.

Introduction

The powder metallurgy enables to produce a high quality parts close to final dimensions and in addition with refined microstructure as compared with those made by the conventional ingot metallurgy. Ball milling process applied before the compaction allows to obtain a very fine microstructure and to extent the solid solubility limits of the elements in the alloys (Suryanarayana 2001). The polycrystalline Co-Ni-Al alloys are considered as an alternative to a single crystalline Ni-Mn-Ga alloys for a magnetic shape memory (MSM) application (Wilson et al., 2007). The maximum deformation which can be achieved in Co-Ni-Al alloys being in external magnetic field is close to 6% and is lower than in Ni-Mn-Ga (~10%) (Ullako et al., 1997). Directional solidification methods have been employed as an effective way to produce well known polycrystalline MSM in Ni-Mn-Ga or Co-Ni-Al alloys with preferred orientations (Liu et al., 2005). There is lack of publication concerning the investigations of MSM alloys obtained by powder metallurgy and this method was applied in the present paper.

In the previous paper (Maziarz et al.) it was shown that ball milling of two Co-Ni-Al alloys with compositions corresponding to the two phase $\beta + \gamma$ region in the ternary Co-Ni-Al phase diagram (Hubert-Protopopescu and Hubert 1992) leads to formation of nanocrystalline fcc Co(Ni,Al) solid solution after 80 hours of milling and a two-phase $\gamma'$ and L1$_0$ microstructure after densification by vacuum hot pressing. In the present paper results of microstructure observations of ball milled and compacted Co-Ni-Al alloys from $\beta$ range are presented.

Experimental procedure

Powders of cobalt, nickel and aluminium of purity 99.8, 99.5 and 99.9 %, respectively, were
used as starting materials. The powders were initially blended to the desired compositions of \(\text{Co}_{28.5}\text{Ni}_{36.5}\text{Al}_{35}\) and \(\text{Co}_{35}\text{Ni}_{30}\text{Al}_{35}\) (in at%) corresponding to the single phase \(\beta\) region in the cross-section of the ternary Co-Ni-Al phase diagram at 900°C. They were prepared under argon atmosphere in a glove-box and subjected to ball milling up to 80 hrs in a Fritsch Pulverisette P5/4 high energy planetary mill. Then, powders were compacted by hot pressing in vacuum (Vacuum Hot Pressing, VHP) under 400 MPa at 700°C for 12 min and additionally annealed at 1300°C in argon for 6 hours followed by water quenching (WQ). The structure investigations were performed using Philips PW 1830 diffractometer with CoK\(\alpha\) radiation, and Philips CM 20 transmission electron microscopy (TEM) equipped with a Phoenix energy-dispersive X-ray analysis system or using Tecnai G2 FEG for high resolution (HREM). The thin foils for TEM observations from milled powders embedded in resin were prepared by cutting of thin slices using Leica microtom, whereas from compacted samples were prepared using Focused Ion Beam (FIB) method.

Results and discussion

The same phase transformations during milling were observed in both investigated alloys. Fig. 1 presents a set of X-Ray diffraction patterns of \(\text{Co}_{28.5}\text{Ni}_{36.5}\text{Al}_{35}\) powders after different milling times. Formation of amorphous phase in the milled powders was already observed after 20 hours of milling manifested by disappearing of peaks originating from pure elements and formation of a one broad peak in 2\(\theta\) range between 40 and 60°. The elongation of milling time causes further amorphization of alloys being almost completed after 80 hours of milling. In order to check the structure and chemical composition of 80 hours milled powders TEM investigations were performed. Fig. 2 presents HAADF image and corresponding bright field (BF) image of individual particle of \(\text{Co}_{28.5}\text{Ni}_{36.5}\text{Al}_{35}\) alloy milled for 80 hours. The average chemical composition of the particulate particles was determined by EDS measurements for several particles of each alloys. The measured mean composition of \(\text{Co}_{28.5}\text{Ni}_{36.5}\text{Al}_{35}\) and
Co$_{35}$Ni$_{30}$Al$_{35}$ powders was: Co$_{28.5}$Ni$_{36.9}$Al$_{34}$Fe$_{0.6}$ and Co$_{33.5}$Ni$_{31}$Al$_{35.1}$Fe$_{0.4}$ (at. %) respectively. The minor contamination by Fe of maximum 0.6 at. % was observed. Such level of Fe contamination is usually observed during ball milling process when both, steel balls and containers are used. One can see that measured composition is very close to that of initial blended mixture of elemental powders. It means that the milling process allowed to produce very homogenous alloys in the powder form. In order to prove the presence of the amorphous structure observed earlier using X-Ray diffraction method after 80 hours of milling, the selected area diffraction pattern (SADP) and dark field techniques were applied. Fig. 3 presents BF, DF and SADP images of Co$_{28.5}$Ni$_{36.5}$Al$_{35}$ powder milled 80 hours. Besides of high intensity diffused ring in the SADP image corresponds to the amorphous matrix, also a weaker rings can be distinguished, indicating presence of some crystalline phase. DF image taken using a high intensity ring for image formation, shows individual crystallites of size below 10 nm. Measurements of diameters of rings allowed to calculate interplanar spacing of nanocrystals. Taking into account the ternary phase diagram (Hubert-Protopopescu and Hubert 1992) three structures can be expected in the investigated alloys. Their lattice parameters and interplanar spacing are given in the Table 1. Comparing the results obtained from SADP with these inserted in Table 1, two phases L$_{10}$ or L$_{12}$ can be considered as that nanocrystals. In order to confirm these results the HREM investigations were performed. Fig. 4 presents the HREM image and corresponding fast Fourier transforms (FFT) and filtered inverse fast Fourier transform (IFFT) taken from 80 hours milled Co$_{28.5}$Ni$_{36.5}$Al$_{35}$ powder. FFT inserted in the right corner was constructed from whole HREM image and shows several rings similar to these presented in Fig. 3 in the SADP image. However in the HREM image individual nanocrystal as cross lattice fringes can be also distinguished. The FFT image taken from nanocrystal marked by square in HREM image shows individual diffracted spots. The measured distances and angle between them were 1.91, 2.06 and 57° respectively. Theoretical
interplanar distances between (111) and (200) planes of L1ₐ phase are 1.94, 2.06 and angle between them 57.81° while for L1₂ 1.79, 2.06 and 54.7° respectively. It can be therefore concluded that this diffraction pattern corresponds to (200) and (111) planes of L1ₐ phase at [011] zone axis orientation. Summarizing, the microstructure observations in TEM allowed to identify a mixture of amorphous phase and L1ₐ nanocrystals in 80 hours milled samples. The origin of tetragonal L1ₐ structure can be explained as deformation induced martensite during ball milling, where the high stresses occurs due to high and frequent collisions between balls.

VHP of milled powders under 400 MPa at 700°C for 12 min resulted in the formation of compacts with a density of about 70% of the theoretical one. An additional heat treatment at 1300°C for 6 hours followed by WQ increased the density significantly and promoted a parent phase which undergoes a martensitic transformation. Unfortunately, the heat effects corresponding to this transformation observed using DSC heating and cooling cycles were small and broad. Therefore, the TEM observation of VHP samples was performed in order to explain whether a martensite structure exists or not. Fig.5 shows the BF and SADP images of VHP Co₃₅Ni₃₀Al₃₅ alloy. Two phase structure B₂ and γ’ can be distinguished, when solving the diffraction patterns corresponding to the [001]B₂ and [321]γ’ zone axes respectively. The B₂ grains are almost equi-axed and their mean size is close to 300 nm. The γ’ grains are larger and attain the size of 1µm and also possess the equi-axed shape. The martensite of L1ₐ structure was not observed, but thermal effects visible in the DSC curves suggest their presence, so they were not found in thin foils or due to significant amount of oxides the Mₛ temperature was shifted to lower temperature due to change of composition of alloys. Therefore it should be placed emphasis on elimination the oxidation process during production of alloys by powder metallurgy methods.

Conclusions
1. Ball milling process of elemental powders with Co$_{28.5}$Ni$_{26.5}$Al$_{35}$ and Co$_{35}$Ni$_{30}$Al$_{35}$ compositions effected in the formation partially amorphous structure after 80 hours of milling.

2. TEM and HREM observations of 80 hours milled powders revealed nanocrystals in amorphous matrix of size close to 5 nm with the L10 structure what is identified as deformation martensite. HAADF technique combined with EDS measurements allowed to define the chemical composition of milled powders as very close to that of the initial blend.

3. Hot pressing in vacuum of milled powders under 400MPa at 700°C for 12 min resulted in formation of compacts with a density of about 70%, being improved by an additional heat treatment at 1300°C.

4. A two-phase B2 and γ’ microstructure with mean grain size close to 500 nm was observed in heat treated samples but also significant contamination by oxides, what can influence the occurrence of a martensitic transformation.

Acknowledgements

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References


strain of directionally solidified ferromagnetic shape memory CoNiAl alloys. *Scripta Materialia* 53, 29-33


Table 1. Lattice parameters and interplanar spacing of B2, L1₀ and L1₂ structures

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<tr>
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<th>B2 (a=b=c=2.85)</th>
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Fig. 1. Set of diffraction patterns of Co28.5Ni36.5Al35 powder after different milling times.
79x48mm (300 x 300 DPI)
Fig. 2. HAADF image and corresponding bright field (BF) image of individual particle of Co28,5Ni36,5Al35 alloy milled 80 hours (marked pints indicates the areas of chemical composition measurements).
79x38mm (300 x 300 DPI)
Fig. 3. BF, DF and SADP images of Co28,5Ni36,5Al35 powder milled 80 hours.
80x78mm (300 x 300 DPI)
Fig. 4. HREM image and corresponding fast Fourier transforms (FFT) and filtered inverse fast Fourier transform (IFFT) of 80 hours milled Co28.5Ni36.5Al35 powder.

156x125mm (150 x 150 DPI)
Fig. 5. BF and SADP images of VHP Co35Ni30Al35 alloy.
80x119mm (150 x 150 DPI)