EVOLUTION OF THE MICROSTRUCTURE AND MAGNETIC PROPERTIES OF A COBALT-SILICON-BASED ALLOY IN THE EARLY STAGES OF MECHANICAL MILLING

RAZVOJ MIKROSTRUKTURE IN MAGNETNIH LASTNOSTI ZLITINE Co-Si V ZAČETNEM STADIJU MEHANSKEGA LEGIRANJA

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The early stages in the mechanical alloying of amount fractions $x = 40$ % cobalt (Co) and $x = 60$ % silicon (Si) powders were investigated using X-ray diffractometry (XRD), scanning electron microscopy (SEM), differential thermal analysis (DTA) and vibrating-sample magnetometry (VSM). After 2–8 h of ball-milling, the characteristic XRD peaks of the face-centered-cubic (fcc) Si and hexagonal close-packed (hcp) Co phases remained sharp without a cobalt-silicide phase. As the milling progressed, the particle size observed by SEM tended to reduce, being accompanied by smoother edges and a narrow size distribution. On the DTA curves, between 200 °C and 1200 °C, exothermic peaks indicated a ferromagnetic-to-paramagnetic transition, whereas endothermic peaks corresponded to the lattice recovery, the transition from a hcp to a fcc Co and melting. The longest milling of up to 8 h significantly increased the magnetic squareness and the coercive field.

Keywords: Co-Si alloys, ball milling, XRD, VSM, DTA

Preiskovan je bil začetni stadij mehanskega legiranja zlitine, sestavljene iz prahov z množinskim delom $x = 40$ % kobalta (Co) in $x = 60$ % silicija (Si). Uporabljena je bila rentgenska difraktometrija (XRD), vrstična elektronska mikroskopija (SEM), diferencialno termična analiza (DTA) in vibracijska magnetometrija vzorcev (VSM). Po mletju od 2 h do 8 h v krogličnem mlinu so še ostali ostri značilni XRD-vrhovi faz fcc Si in hcp Co brez Co-silicidne faze. S podaljševanjem časa mletja se s SEM opazi zmanjšanje velikosti delcev prahov, zožanje njihove velikostne porazdelitve in povečanje zaobljenja robov delcev. Na DTA-krivuljah se je med 200 °C in 1200 °C pojavil eksotermni vrh, ki je posledica prehoda iz feromagnetne v paramagnetno fazo, endotermni vrh pa je posledica poprave rešetke zaradi prehoda iz hcp v fcc Co in nato taljenja. Najdaljši časi mletja (do 8 h) pomembno vplivajo na magnetno koercitivnost in povečanje kvadratičnosti histerezne zanke.

Ključne besede: zlitina na osnovi Co-Si, kroglično mletje, XRD, VSM, DTA

1 INTRODUCTION

Mechanical milling has been successfully used in producing a variety of magnetic amorphous alloys, intermetallic compounds, nanocomposites and nanocrystalline powders.[1,2] Milling ferromagnetic powders (i.e., Co, Fe, Ni) with non-magnetic metals (e.g., Au, Cu, Ag) gives rise to mechanical alloys with a giant magnetoresistance (GMR) effect.[3] Since an addition of Si reduces the magnetic anisotropy and the eddy-current loss in commercial steels, Fe–Si mechanical alloys also received much interest.[4–7] By contrast, Co–Si alloys only gained attention in the last decade after being recognized as hydrogen-storage materials for nickel-metal hydride batteries. The discharge capacity and cycling ability of negative electrodes are reportedly improved when using 1 : 1 or 2 : 1 Co–Si milled for 10–80 h.[8–10] In addition to homogenizing their sizes and shapes, the ball milling leads to several compounds as shown by the Co–Si phase diagram.[11] The Co_2Si, $CoSi$ and $CoSi_2$ phases affect the magnetic and hydrogen-storage properties of the alloys.[10–14]

In this work, the evolution of the phases during the initial period of the milling of Co with $x = 60$ % Si is examined. The thermal and magnetic properties of these Co–Si powders from the early stage of the ball-milling for up to 8 h are also reported.

2 EXPERMENTAL WORK

Elemental crystalline cobalt powder (a 99.8 % purity with the average particle size of less than 2 μm) and silicon powder (a 99 % purity with the average particle size of less than 44 μm) were mixed in an atomic ratio of 40 : 60 in a steel vial loaded with steel balls of 3 mm in diameter. The ball-to-powder mass ratio was around 15 : 1. The vial was spun at 595 r/min on a vario-planetary mill (Fritsch) for (2, 4, 6 and 8) h in a dry condition under air. The structural and magnetic properties of the milled powders were characterized with X-ray diffrac-

tion (XRD) using Cu-$K\alpha$ radiation and vibrating sample magnetometry (VSM), respectively. The coercive field was determined from the x-intercept of the hysteresis loop obtained with VSM, whereas the y-intercept corresponded to the remanent magnetization. A ratio of the remanent magnetization to the saturation magnetization is referred to as the magnetic squareness in **Table 1**. The thermal properties were studied using a differential thermal analysis (DTA) with a heating rate of 5 °C min^{-1}.
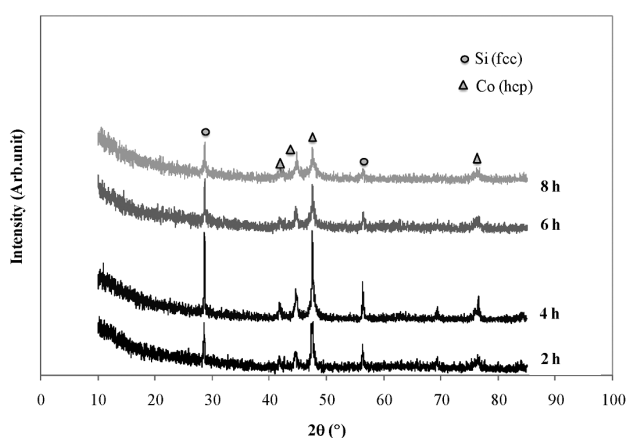
Table 1: Magnetic squareness and coercive field of Co – x(Si) = 60 % powders
Tabela 1: Magnetna kvadratnost in koercitivno polje prahov iz Co – x(Si) = 60 %

Milling time (h)	Magnetic squareness	Coercive field (kA m^{-1})
2	0.28	15.15
4	0.29	15.32
6	0.28	15.48
8	0.37	19.41

3 RESULTS AND DISCUSSION

The XRD patterns of the Co–Si powders after the milling shown in **Figure 1** have characteristic peaks of the fcc Si phase ($2\theta = 28.440$ °, 47.300 ° and 56.120 °) and the hcp Co phase ($2\theta = 47.220$ °, 44.080 ° and 41.440 °). According to the literature[15], allotropic Co undergoes a transition from the hcp to the fcc structure at a temperature around 450 °C. Previous works suggested that the ball milling can also induce such an allotropic transformation by virtue of a defect accumulation.[16–19] The mixed phase may be converted into a highly distorted hcp structure in the early stage of milling but further milling leads to a fcc structure as a result of the stacking faults from the plastic deformation.[17] The CoSi and CoSi$_2$ phases are not clearly detected. The formation of silicide compounds generally requires prolonged milling and, as demons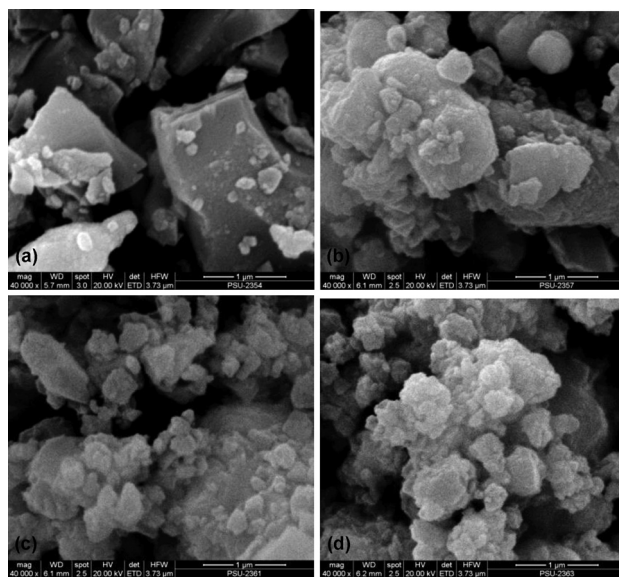trated with Pd–Si[1], it is dependent on the volume fractions of the two elemental powders. In some cases, the milling is carried out at a high temperature to stimulate the formation of compounds.[1] In our case, all Co and Si peaks are rather sharp indicating a high degree of crystallinity. However, the peaks clearly broaden and their intensities are decreased after the milling for 8 h. The small peaks of Si slightly below 70 ° in the case of milling for 2 h and 4 h disappear after the longer milling.

The morphologies of the Co–Si powders at various milling times obtained with SEM are shown in **Figure 2**. After the milling for 2 h, several particles are still bulky, with straight and sharp edges. The edges are gradually broken or rubbed off and the particles become smoother as the milling progresses. Furthermore, the particle size is clearly reduced after the longest milling time of 8 h. It was also reported that a decrease in the particle size of Fe–Si powders began to be noticeable only after 5 h of ball milling.[7] It is known that milling modifies the size of ball-milled powders by virtue of fracturing and cold welding. Each process dominates in a different stage of milling and the welding of particles is dominant in the initial milling time of up to 3 h.[5,6] The narrower size distribution seen in the case of 8 h milling is a result of simultaneous fracturing of larger particles and cold welding of smaller particles. The powder from the early stage of milling can be modeled as brittle Si embedded in more ductile Co particles.

It is seen from the DTA curves in **Figure 3** that after 2 h to 8 h of milling, the samples exhibit a broad exothermic peak centered around 600 °C. The area is increased with the milling time because more energy is released in the case of prolonged milling. Another exothermic peak is observed that was shifted from above to

Figure 1: XRD patterns of Co – x(Si) = 60 % powders after milling for 2–8 h
Slika 1: XRD-posnetki prahov Co – x(Si) = 60 % po mletju od 2 h do 8 h

Figure 2: SEM micrographs of Co – x(Si) = 60 % powders after milling for: a) 2h, b) 4h, c) 6h and d) 8 h
Slika 2: SEM-posnetki prahov Co – x(Si) = 60 % po mletju: a) 2 h, b) 4 h, c) 6 h in d) 8 h
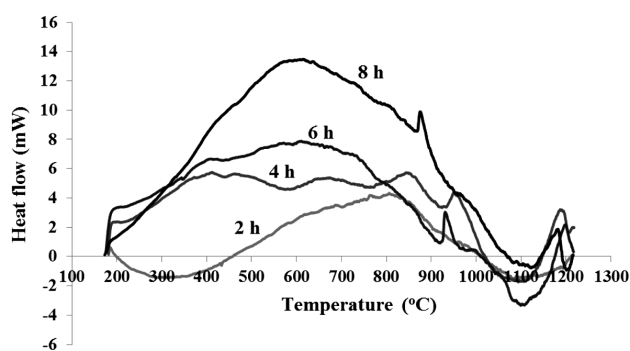
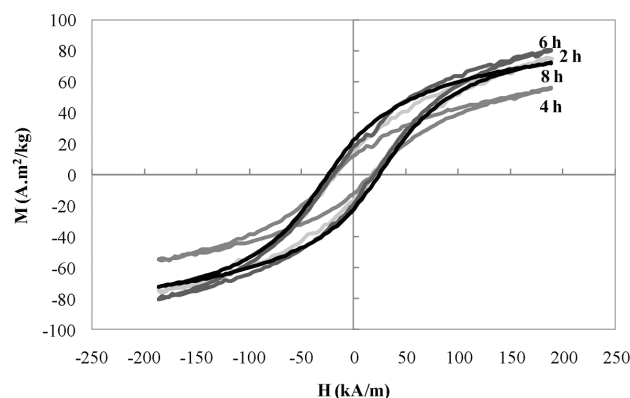**Figure 3:** DTA curves of Co – x(Si) = 60 % powders after milling for 2–8 h
Slika 3: DTA-krivulje prahov Co – x(Si) = 60 % po mletju od 2 h do 8 h

Figure 4: Hysteresis loops of Co – x(Si) = 60 % powders after milling for 2–8 h
Slika 4: Histerezne zanke prahov Co – x(Si) = 60 % po mletju od 2 h do 8 h

below 900 °C due to the increase in the milling time. This small exothermic peak may correspond to the ferromagnetic-to-paramagnetic transition. In addition to both exothermic peaks, there are endothermic peaks at around 1100 °C corresponding to the melt appearing in the system and at around 450 °C resembling the transition from hcp to fcc in bulk Co.[15] The latter is less notable in the case of a longer milling time because the defect accumulation due to milling already facilitates the transformation to the fcc phase. The heat absorption also reduces the defect and dislocation density in the lattice-recovery process at around 200–300 °C which is clearly detected only in the case of 2 h milling.

The hysteresis loops of the milled Co–Si powders are shown in **Figure 4** and their magnetic parameters are summarized in **Table 1**. Like the other granular Co alloys[3], the magnetization is not saturated under the magnetic field of about 200 kA m^{-1}. Both the coercive field and squareness (approximated from the ratio of the remanence to the maximum magnetization in 200 kA m^{-1}) remain rather constant in the case of 2–6 h milling but increase significantly after the milling for 8 h. Interestingly, the size of Co particles is slightly modified during the 2–6 h milling. This can then be related to the dependence of the magnetic properties on the particle size of magnetic mechanical alloys. The coercive field is also related to the lattice imperfections as the milling is progressed because they impede the domain-wall movement.[4,5] Although Co has a strong crystalline anisotropy[20], it is noted that these coercive-field values are comparable to those of the Fe alloys with a high fraction of Si, which could be further reduced with heat treatments.[5,7]

4 CONCLUSION

The ball-milling of Co – 60 % Si for up to 8 h does not significantly induce silicide and amorphous phases. However, there are some modifications in the morphology and particle size during this early stage of milling. As a result, the thermal and magnetic properties of Co–Si powders are considerably influenced by the milling time. In addition to the endothermic DTA peaks corresponding to the lattice recovery, the allotropic Co transition, the melting and the ferromagnetic-to-paramagnetic transition give rise to an exothermic peak, which shifts to a lower temperature as the milling progresses. The considerable reduction in the particle size after the milling for 8 h results in an enhanced coercive field and magnetic squareness.

Acknowledgements

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