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Growth Process and Magnetic Property of Ferromagnetic Nanocluster Rods

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[Abstract] In a one-pot-fabrication at room temperature, both an iron-neodymium-dysprosium-boron permanent magnet ($Fe_{66}Nd_{28}Dy_4B_1$) and cobalt (Co) metal have been directly converted into the corresponding ferromagnetic nanometer scale cluster (nano-cluster) rods using pulsed laser ablation combined with magnetic field trapping. The morphology of the produced nano-materials was analyzed by electron microscopy and the composition by electron energy loss spectroscopy, and it was found that 1-D structured soft-magnets up to ~ 150 nm length consisting of magnetic clusters a few nanometers in diameter. The mechanism and driving behind their growth process and their magnetic evolution have been proposed.

[Experimental Section] Experimental set-up consists of two parts: a laser ablation chamber with an inlet for the carrier gas and a side arm with a magnetic field. At the side arm, a pair of commercial permanent magnets (surface magnetic flux strength: 1.22 T) were diagonally attached to the direction of the gravity to provide a magnetic flux strength of ~ 0.5 T at the center. As the laser target, we used either a iron-neodymium-dysprosium-boron permanent magnet ($Fe_{66}Nd_{28}Dy_4B_1$; Edmund, purity: 99%) or Co metal (Nilaco, purity: 99.99 %). With irradiation of the focused 532 nm photons of Nd^{3+}:YAG laser onto the target, metal aggregates were generated around the plume, and transported into the magnetic field zone by the flowing argon (Ar) gas. Since the superparamagnetic or ferromagnetic nano-clusters (NCs) were effectively caught by the strong magnetic field, they were piled up linearly along the magnetic field lines. The typical laser energy was ~15 mJ/pulse at a repetition rate of 10 Hz. The ambient Ar pressure was 600 ~ 700 Torr, and the flow rate was 110-130 ml / min.

[Results and Discussion] Figs. (a)-(h) show a growth evolution of the NCR of Co metal with changes in the deposition time from 1 to 15 hours. As indicated by arrows in Figs. (a) and (b), Co NCs begin to aggregate themselves onto the graphite of the TEM grid along the lines of the magnetic field. Then, they pile up linearly as the deposition time increases from ~ 1 to ~ 7 hours (Figs. (c) - (e)). These Co NCRs remain linear to a size of ~ 150 nm up to a deposition time of ~ 7 hours. Interestingly, the diameters of the Co NCRs, ranging from 10 to 20 nm**,** change little during their growth. This shows that the main process is growth in length rather than in diameter. After ~ 9 hours, however, the assembly of NCs no longer maintains its linearity, and some branches, marked as arrows in Fig. (f), begin to grow from the side of the main backbone. In addition to the HR-TEM images, the scanning electron microscope (SEM) images clearly show many branched NCRs having a diameter of ~ 20 nm after ~ 9 hours of deposition; Fig. (g) illustrates the Co and Fig. (i) the $Fe_{67.6}Nd_{26.8}Dy_{3.2}B_{2.3}$. After ~ 15 hours of deposition, a unique micrometer-scale aggregation of NCs (MANC) is generally found for both Co (Fig. (h)) and $Fe_{67.6}Nd_{26.8}Dy_{3.2}B_{2.3}$ (Fig. (j)). As shown in Figs.

(c)-(e), both the uneven and the filled morphology of the NCRs indicate that the melting process during collisions induces bond formation between building blocks of NCs, where NC's possess a lower melting temperature and this enhances bond formation. This partial coalescence results in their ferromagnetic behavior as soft-magnets. The branched structures of the NCRs and the MANCs stems from the fact that the NCRs are continuously shaken by the flowing Ar. Since the amount of shaking seemingly becomes larger, as the NCR lengthens**,** the shaking movement can reasonably allow the NCs to be piled up at the side position of a NCR as well as at the top position. Judging from the images, the branched structure appears when the length of a NCR exceeds ~ 150 nm. Moreover, a mutual aggregation of several branched NCRs may occur, resulting in a bundle of them at the micrometer-scale. Specifically, with an increase in the length of the NCR, the enhancement factor of $4\pi \boldsymbol{M}_{NCR}$ results in more and more growth of larger aggregates of the MANCs. Note that if micrometer or millimeter Fe powders are scattered onto inter-magnets**,** we can also observe lines of aggregated Fe powders on the millimeter-scale. In other words, the growth process is proposed to be an aggregation of NCs → short NCRs → long NCRs → branched NCRs → MANCs. Furthermore, whole growth process, driving force for linear growth, magnetic property for Co and $Fe_{67.6}Nd_{26.8}Dy_{3.2}B_{2.3}$ NCRs, and magnetic evolution for one-dimensional Co nanostructures will be discussed.

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