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ABSTRACT

We have investigated the structural and magnetic properties of $Co_{1-x}V_x$ nanoparticles (NPs) with composition x = 0.25 (stoichiometric) and 0.29 (under-stoichiometric) prepared by the cluster-beam deposition (CBD) technique. Our data shows that the as-made $Co_{1-x}V_x$ NPs are a mixture of the high-temperature phase (HTP) and the low-temperature phase (LTP) of Co_3V and the particles are superparamagnetic at room temperature (RT) with blocking temperatures (T_B) of 90 and 137 K for x = 0.25 and 0.29, respectively. This behavior contrasts with the bulk which are paramagnetic down to 4.2 K. When the $Co_{75}V_{25}$ NPs are annealed at 573 K, they undergo a phase separation into a mixture of phases and become ferromagnetic at room temperature with Curie temperature (T_c) of 515 K.

INTRODUCTION

Bulk intermetallic compounds have attracted much attention in many different materials because of their interesting physical properties and technological applications.[1–4] Nanoparticles (NPs) of intermetallic compounds have shown interesting physical properties due to both size and surface effects. There are numerous reports where the magnetic properties of NPs are superior when compared to those corresponding of bulk alloys. For example, Co_2Si nanoclusters have been reported to have moment-enhancement as compared to the bulk alloy.[5] Also, Tosun *et al.*[6] reported that nanoclusters of Co_2Ge are ferromagnetic at room temperature with Curie temperature (T_c) of 815 K in contrast to that of bulk which is ferromagnetic only at cryogenic temperatures.[7]

The stoichiometric intermetallic Co_3V compound exists in two structures, an ordered hexagonal (Al_3Pu-type) low-temperature phase (LTP) and a cubic $L1_2$ (Cu_3Au)-type high-temperature phase (HTP). Both the LTP and HTP in bulk alloys are reported to be paramagnetic down to 4.2 K.[8,9] The same authors reported weak ferromagnetism near 4.2 K in Co-V alloys at stoichiometric and under-stoichiometric the LTP, possibly due to disordering when Co atoms occupy V lattice sites. The alloys at the Co-rich side of the LTP, however, were reported to have very large magnetic moments (larger than the Co magnetic moment of 1.72 μ_B) which may be attributed to the polarization of neighboring Co atoms by the excess magnetic Co atoms on the V lattice sites.[8] The polarization was explained to occur because "Co atoms with eight or less Co nearest neighbors are non-magnetic as well as the V atoms, in contrast to the magnetic Co atoms with nine or more Co nearest neighbors."[8]

Because of the interesting magnetic properties of bulk Co-V alloys, we decided to fabricate NPs $Co_{1-x}V_x$ NPs with x = 0.25 and 0.29 and investigate the effects of particle size and disorder on their structural and magnetic properties. To the best of our knowledge, there is no such study on $Co_{1-x}V_x$ NPs.

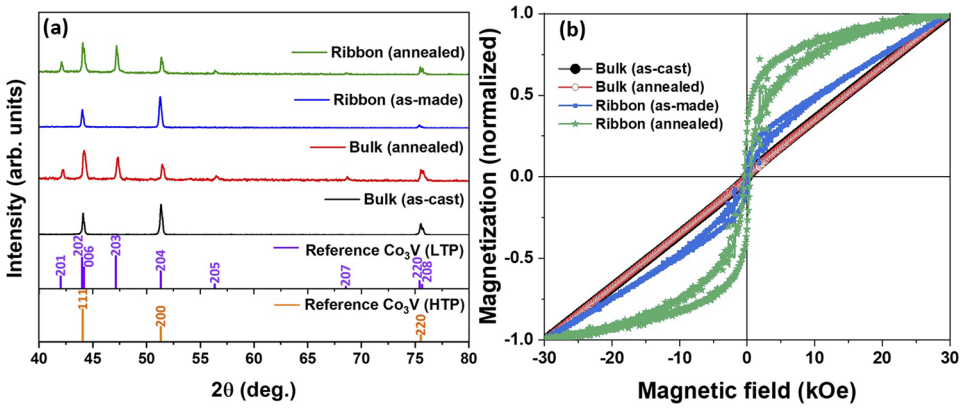

FIG. 1. (a) X-ray diffraction (XRD) data of the bulk and ribbon Co_3V samples with the reference high-temperature phase (HTP) and low-temperature phase (LTP) lines, (b) Hysteresis loops of the bulk and ribbon samples at 300 K.

EXPERIMENTAL METHOD

The cluster-beam deposition (CBD) technique, which was described elsewhere,[10] was used to synthesize $Co_{1-x}V_x$ NPs. The NPs were prepared with 1.4 Torr Ar pressure and 70 W sputtering DC power from a solid sputtering target with 75 at. % Co and 25 at. % V. They were deposited on Si wafers and C-coated Cu grids for magnetic, structural and microstructural analyses. For comparison purposes, melt-spun ribbons were made at a wheel speed of 45 m/s. The crystal structure analysis was carried out with a Rigaku X-ray diffraction (XRD) diffractometer using Cu Kα radiation with a wavelength of 1.540 Å. The microstructure and electron diffraction were made with a JEOL 3010 transmission electron microscope (TEM) operating at 300 kV. The volumes fraction of the nanoparticulate films were obtained with a JEOL 6330F scanning electron microscope (SEM) and the compositional analyses

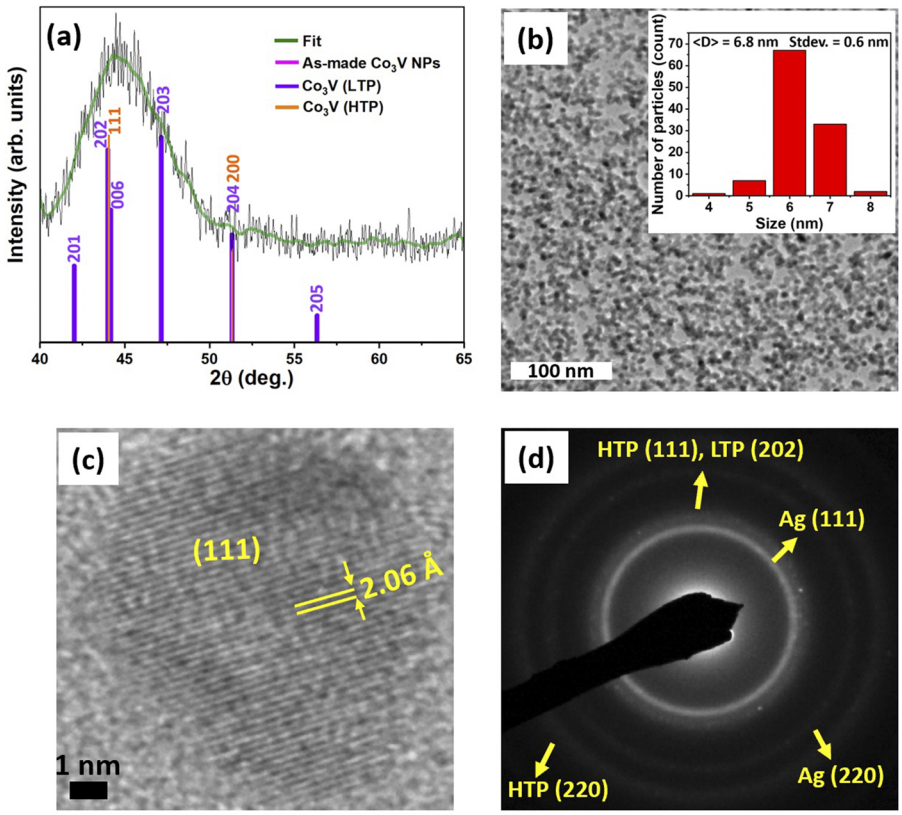

FIG. 2. (a) XRD pattern of the nanoparticles (NPs) with the reference HTP and LTP Co_3V lines, (b) Transmission electron microscope (TEM) micrograph showing NPs with an average size of 6.8 nm with the inset showing the size distribution, (c) High-resolution TEM (HRTEM) (d) Selected area diffraction (SAD) images of the NPs.

were done with energy dispersive X-ray spectroscopy (EDS). Magnetic measurements were made with a Quantum Design Versa Lab vibrating sample magnetometer (VSM).

RESULTS AND DISCUSSION

As-cast bulk and melt-spun ribbons of Co_3V were found to have the cubic HTP structure.[8,9] When both the bulk and ribbon samples were annealed, they were found to exhibit the ordered hexagonal LTP.[8,9] Fig. 1a shows the XRD data of the as-made and annealed samples as well as the reference LTP and HTP XRD patterns.[8,11] The lattice parameter of the as-made bulk is a = 3.564 Å and for the annealed a = 5.020 Å, c = 12.260 Å. As-made ribbons have a = 3.562 Å and the annealed a = 5.032 Å, c = 12.300 Å. These values are close to the values reported by Y. Aoki *et al.*[8,11]

The as-made and annealed ribbons exhibit some weak ferromagnetism at room temperature (Fig. 1b) which may be due to introduction of disorder in the ribbons during melt-spinning unlike both the HTP and LTP of bulk alloys $Co_{1-x}V_x$ with $0.241 \leq x \leq 0.301$ which are paramagnetic above 4.2 K as reported by Y. Aoki *et al.*[8,9]

The as-made NPs of $Co_{1-x}V_x$ with x = 0.25 and 0.29 were found to have an average size of 6.8 nm and 6.3 nm, respectively. In this article, the structural analyses of the as-made $Co_{1-x}V_x$ NPs with x = 0.25 (Co_3V) are only presented. According to our Rietveld refinement analysis, the as-made NPs have 85 vol. % of the HTP and 15 vol. % of the LTP (Fig. 2a). The lattice constant of the HTP was determined to be a = 3.545 Å which is slightly smaller than that of bulk. Figure 2 shows the XRD, TEM, HRTEM, and SAD data for the as-made NPs. Both the XRD and TEM results suggest that the as-made NPs are a mixture of small and disordered/partially ordered particles. Fig. 2c shows a HRTEM image of the as-made NPs with a d-spacing value of 2.06 Å which could be fitted to the (111) reflection of the HTP and (202) of the LTP.

Thermomagnetic data (Fig. 3a) show that the $Co_{1-x}V_x$ NPs with x = 0.25 and 0.29 are superparamagnetic at RT with blocking temperatures (T_B) value of 137 K (Fig. 3a) and 90 K (not shown here), respectively. Saturation magnetization (M_s) values of the NPs with x = 0.25 (Fig. 3b) and 0.29 at 300 and 50 K are found to be (119 emu/cm^3, 140 emu/cm^3) and (83 emu/cm^3, 95 emu/cm^3), respectively. The M_s values at both temperatures increase with Co concentration as shown in (Fig. 3c). The effective anisotropy constant values (K) of the NPs at 50 K have been determined by fitting the magnetization data to the law-of-approach to saturation[12,13] and they have been determined to be 1.8 and 0.4 Merg/cm^3 for x = 0.25 and 0.29, respectively. The coercivity (H_c) values which are 0.21 and 0.16 kOe for x = 0.25 and 0.29, respectively (inset of Fig. 3b) and they follow the increasing trend of K. Possible surface effects and the existence of the LTP in the as-made NPs may be the reason of the anisotropy.

The high temperature thermomagnetic measurements (Fig. 3d) show that the magnetization of the as-made NPs increases at 360 K. When the temperature is increased to 573 K and the sample is cooled to RT, the sample is now ferromagnetic. The as-made samples were

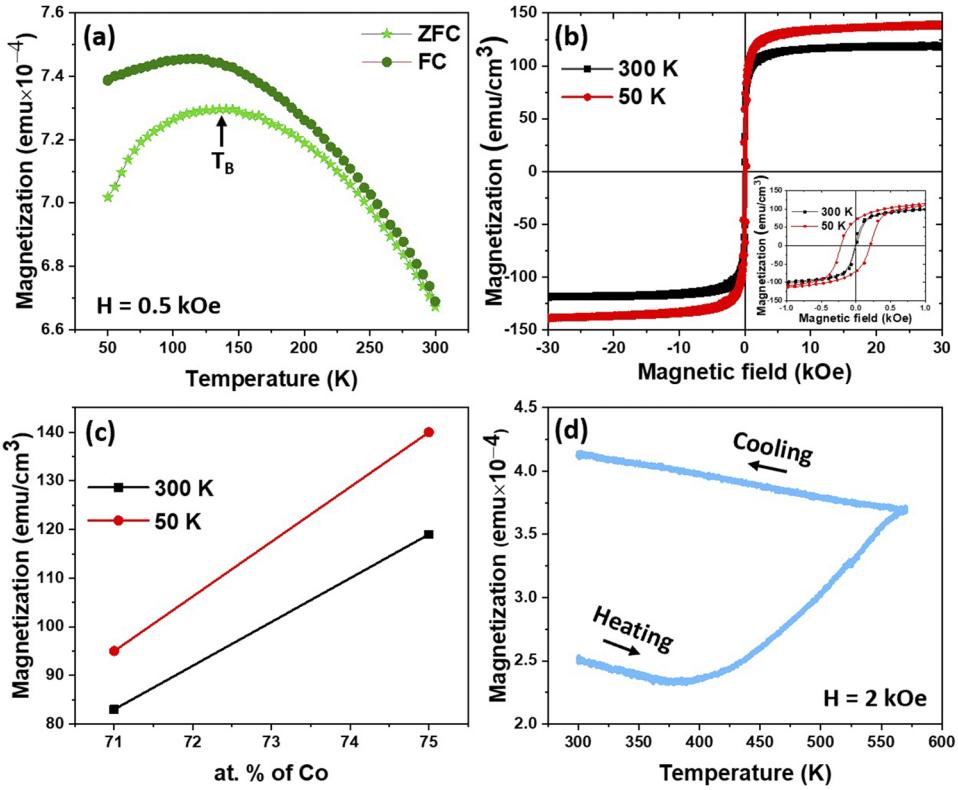

FIG. 3. (a) Zero-field-cooled (ZFC)-Field-cooled (FC) magnetization curves at 0.5 kOe Oe for x = 0.25, (b) Hysteresis loops at 300 and 50 K for x = 0.25, (c) Saturation magnetization (M_s) at 300 and 50 K versus at. % of Co, (d) High temperature thermomagnetic $M(T)$ curves at 2 kOe for x = 0.25.

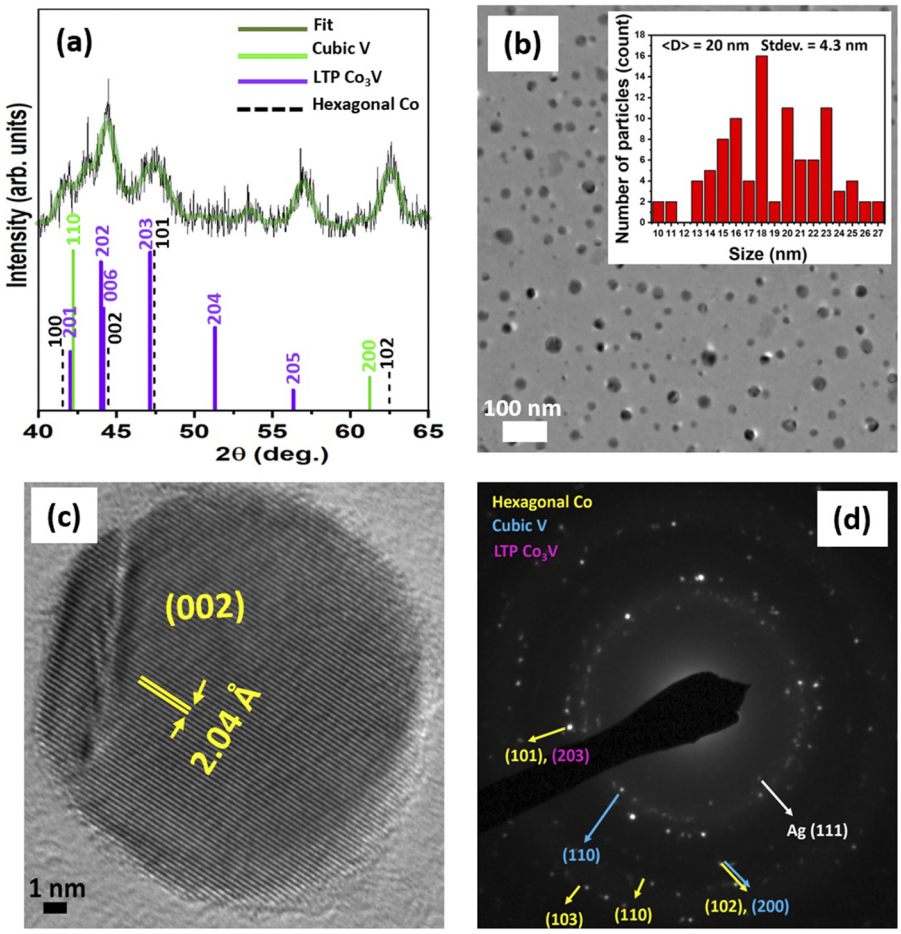

FIG. 4. Structural properties of the annealed Co_3V NPs: (a) XRD pattern of the NPs with the reference LTP Co_3V, hexagonal Co-V[14] and cubic V-rich Co solid solution[15] lines, (b) TEM, (c) HRTEM 2.04 Å which could be fitted to the (002) reflection of the hexagonal Co, (d) SAD images of the NPs.

then annealed at 573 K in order to investigate whether the increase in the magnetization could be due to structural and/or magnetic transformations in the as-made NPs. After annealing, the average size of the NPs increased to 20 nm (inset of Fig. 4b) and the NPs became more crystalline which is clearly observed in the XRD, TEM, HRTEM, and SAD data shown in Figure 4.

Our XRD (Fig. 4a) suggest that the annealed NPs may be a mixture of the LTP Co_3V, hexagonal Co, and cubic V. The presence of a new phase is not excluded because the peak at 62.6° with a relatively high intensity-as compared to the reference patterns-has not yet been clearly identified. All the XRD peaks are shifted to higher angles. A possible explanation for this is the precipitation of cubic

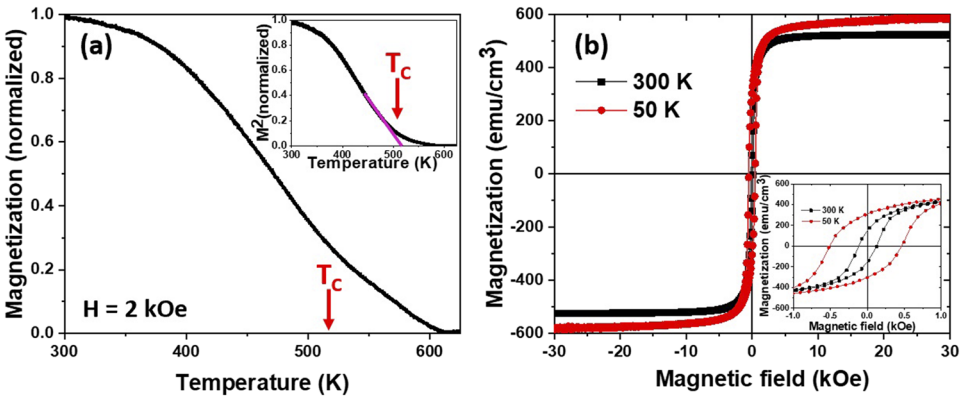

FIG. 5. Magnetic properties of the annealed Co_3V NPs: (a) High temperature thermomagnetic curves at 2 kOe, (b) Hysteresis loops at 300 and 50 K.

V nanoclusters during the phase separation. This makes some of the nanoclusters to be Co-rich which then may be regarded as the hexagonal Co. Such a phase separation in Co_3V alloys was reported by Ustinovshikov.[16] Since the atomic radius of Co is smaller than that of V, the XRD peaks of both V-rich Co and the Co-rich LTP Co_3V clusters also shift to higher angles due to the phase separation.

The annealed NPs are ferromagnetic at room temperature with a T_C = 515 K (Fig. 5a). The inset of Fig. 5a shows the method of determination of the T_C: finding the intersect of the linear part of the M^2 versus T data with the temperature axis. Their M_s values at 300 and 50 K are increased from (119 emu/cm^3, 140 emu/cm^3) to (526 emu/cm^3, 603 emu/cm^3) as shown in Fig. 5b. Their H_c values at 50 K are increased from 215 Oe to 500 Oe which can also be seen in the inset of Fig. 5b. The increase in the H_c values may indicate that the annealed NPs have predominantly the LTP or Co-rich LTP. Their effective anisotropy values, K, at 50 K follow H_c trend and the values are increased from 1.8 Merg/cm^3 to 4.5 Merg/cm^3.

CONCLUSIONS

In conclusion, nanoparticles of $Co_{1-x}V_x$ with x = 0.25 and 0.29 have been synthesized using the gas-aggregation cluster-beam deposition method and their structural and magnetic properties were investigated. The as-made nanoparticles for x = 0.25 and 0.29 were found to be a mixture of the HTP and LTP and are thermally blocked at 50 K unlike the bulk which are paramagnetic down to 4.2 K. It was observed that when nanoparticles are annealed at 573 K, they are a mixture of the LTP Co_3V, hexagonal Co, and cubic V-rich Co. The annealed nanoparticles are ferromagnetic at room temperature with Curie temperature of 515 K. The enhanced properties of the as-made nanoparticles may be attributed to polarization of Co atoms due to magnetic excess Co atoms on the V lattice sites which could occur due to the structure not being completely ordered. This indicates that the Co atoms with increased number of Co nearest neighbor leads to an increase in the Co-Co exchange interaction.

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