Magnetic properties of fine cobalt particles prepared by metal atom reduction

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Ultrafine particles of cobalt were prepared under argon by reduction of cobalt halide solutions in diglyme ether with metallic lithium and a naphthalene catalyst. The fine particles had a particle diameter in the range 50–1200 Å. The size was dependent on the reaction temperature. X-ray diffraction showed crystalline particles of α-Co and CoO. Because the ratio of the metal core to oxidized shell decreases with particle size, the smaller particles displayed much lower magnetization and higher coercivity at low temperature. The anisotropy constant K changes slightly with particle size and has a value close to the bulk value.

INTRODUCTION

Numerous methods exist for the preparation of metal powders. Finely dispersed metal particles can be obtained by reducing metal salts in etheral or hydrocarbon solvents using alkali metals (lithium, sodium, or potassium). Each alkali metal has its own particular advantage. The reactivities and, in some cases, the products are highly dependent on the reduction conditions, e.g., anion, reduction temperature, solvent, etc. This method has played an important role in the development of modern organometallic chemistry.[1] In this study we have used this technique to produce particles from a Co halide solution in diglyme ether using lithium as a reducing agent. The aim of this research is to create fine Co particles with properties different than those obtained from other methods, e.g., borohydride reduction,[2] and to study their magnetic properties and structural morphology.

EXPERIMENTAL METHOD

Cobalt fine particles were prepared by dissolving anhydrous $CoCl_2$ in diglyme ether [Bis (2-methoxyethyl) ether] containing excess naphthalene under an argon atmosphere while adding freshly cut lithium. Vigorous stirring was used. Excess naphthalene was used as a catalyst to ensure rapid and complete dissolution of the lithium. The initially blue mixture slowly darkened over a period of 24 h. A black slurry was formed in a slightly green solution. In some cases the lithium metal was found to be coated with Co metal powder. The slurry was washed by letting it settle, syringing off the supernatant, and then redispersing in fresh glyme. This was repeated a few times until no green color was visible in the solution. Then we used water to remove the diglyme ether. The powder was washed with acetone and then dried under vacuum. In this experiment the $CoCl_2$ concentration was kept constant at 0.026 M and the preparation temperature was changed from $-20\,^\circ\mathrm{C}$ to $120\,^\circ\mathrm{C}$. This led to different reaction rates and therefore different particle sizes.

The magnetic properties were measured with a SQUID magnetometer in the temperature range of 10–300 K and in magnetic fields up to 50 kOe. The crystal structure was examined by x-ray diffraction and the particle size by transmission electron microscopy.

RESULTS AND DISCUSSION

X-ray diffraction patterns showed that all the samples made at different temperatures were crystalline. However, some differences were observed in the phases present when the sample preparation temperature T_p changed, as shown in Fig. 1. At high temperatures such as 80 or 120 °C the

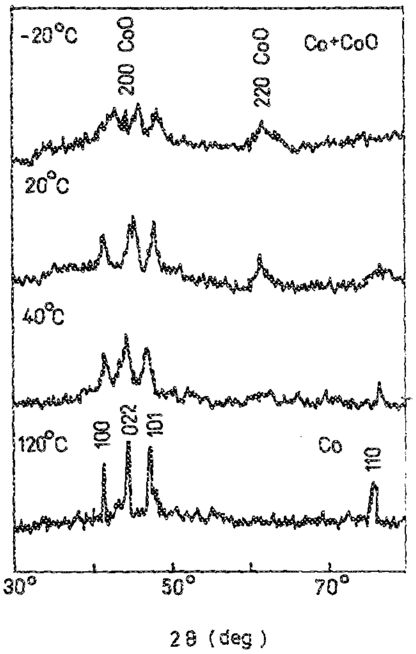

FIG. 1. X-ray diffraction patterns of Co particles prepared at different temperatures.

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powders showed only the α-Co phase, whereas at lower preparation temperatures, αCo + CoO phases were observed. The oxide most likely comes from reaction of the nascent Co particle with the water wash. Figure 2 shows that the size determined by TEM increases with increasing temperature. The x-ray and TEM results can be combined to obtain a simple model for the particle's structure. If we assume a CoO shell of constant thickness resides on the particle surface, one would expect a larger Co/CoO ratio as the size increase. This is what is observed since both the size and Co/CoO ratio increase with preparation temperature.

The saturation magnetization and coercivity as a function of preparation temperature are also shown in Fig. 2. The increase in saturation magnetization is due to the larger particles which, according to our model, have a larger Co/CoO ratio than the smaller particles. The variation of coercivity with preparation temperature is a direct result of the particle size. The highest coercivity at 10 K was obtained with the smallest particles (~ 50 Å).

If the particles are in the single domain range (for Co the single domain size is around 300 Å),[3] there will be a blocking temperature T_B below which the magnetic hysteresis will be stable. The coercivity for such an ideal assembly is given by[3]

$$H_C=\frac{2K}{M_S}\left[1-\left(\frac{25kT}{KV}\right)^{1/2}\right]=\frac{2K}{M_S}\left[1-\left(\frac{T}{T_B}\right)^{1/2}\right],$$

where K is the anisotropy energy density constant, M_S is the saturation magnetization, k is Boltzmann's constant, and V is the particle volume. Therefore, when H_c is plotted vs $T^{1/2}$, the blocking temperature can be found. Figure 3 shows H_c vs $T^{1/2}$. The slope of the curves decreases with increasing preparation temperature. The curves deviate from a straight line near room temperature because there is a particle size distribution in every sample. Using the straight line range extrapolation, we can estimate the blocking temperature T_B. The results are shown in Fig. 3 (insert). The blocking temperature is found to increase with particle size as expected.

The results of TEM, T_B, and H_C indicated that the samples made below room temperature are single domain parti-

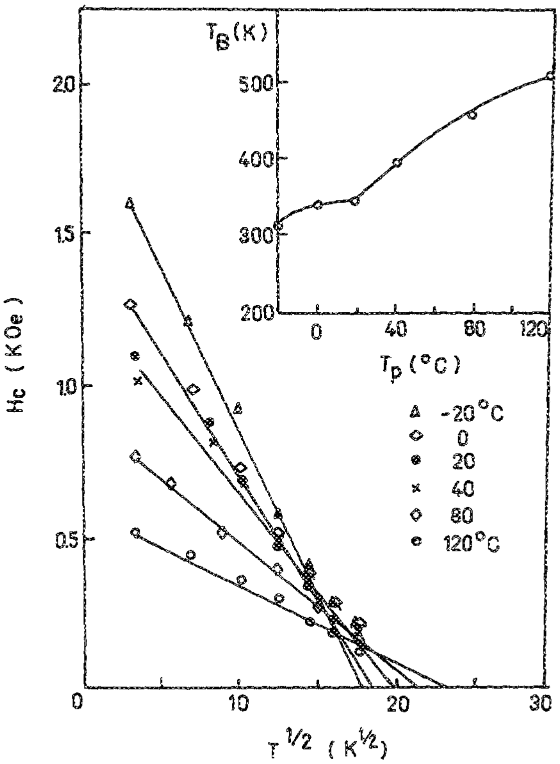

FIG. 3. Temperature dependence of coercivity. Blocking temperature vs preparation temperature (insert).

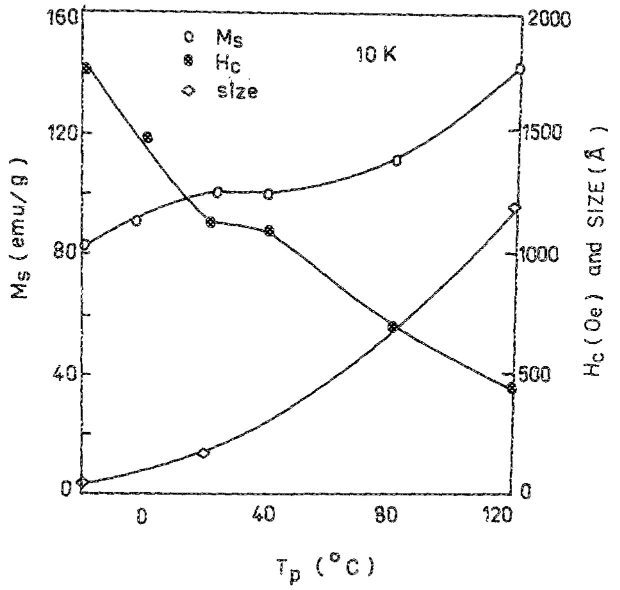

FIG. 2. Coercivity and saturation magnetization as a function of preparation temperature.

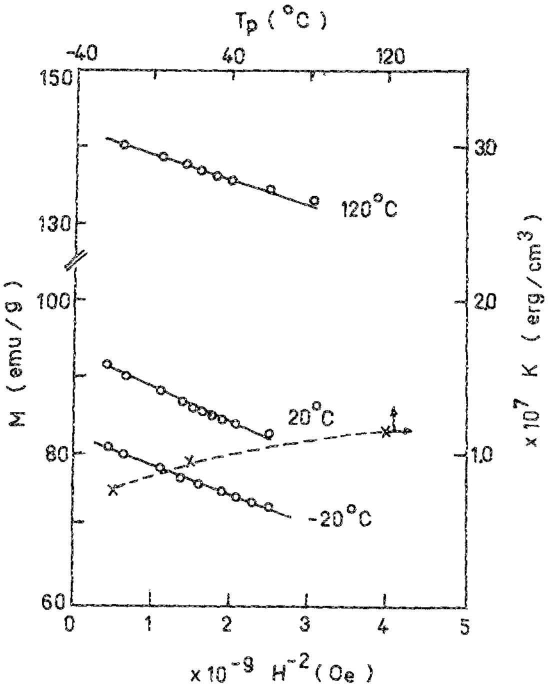

FIG. 4. M vs H^{-2} and the anisotropy constant K as a function of preparation temperature.

cles having a uniaxial anisotropy. The law of approach to saturation[4] was used to determine the anisotropy constant K of the particles by plotting M vs H^{-2} (Fig. 4). The anisotropy constant K was found to change slightly with preparation temperature and is close to the bulk value (Fig. 4).

CONCLUSIONS

We have used alkali metal (Li) reduction of Co cations in glyme to produce small magnetic particles. Particle diameters were dependent on the reaction temperature and could be varied from 50 to 1200 Å. The proposed particle morphology was that of CoO-coated Co core. This would explain the increase in M_S and decrease in H_C as the size increased. Finally, the anisotropy constant shows little change in size and is close to the bulk value.

ACKNOWLEDGMENT

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