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Magnetization-Blocking Process by Volume Development of Ferromagnetic Fine Particles

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Magnetization-blocking process in chemical remanent magnetization was demonstrated through the size development of ferromagnetic precipitates generated by an aging of Cu-Co alloy, the magnetic behaviour of which changes from superparamagnetic to stable single domain and then to a multidomain stage, according to the increase in the size of the precipitates. It has been shown that a remanent magnetization is acquired during the transition from a superparamagnetic to stable ferromagnetic state and that the remanent magnetization thus obtained decreases as a result of the formation of domain walls if the size of the precipitates exceeds the critical single domain grain size. The result can be well explained by Néel's thermal fluctuation theory of single domain grains and domain structure theory of ferromagnetics. The general idea confirmed in the present study has been successfully extended to the chemical remanent magnetization (CRM) phenomena in synthetic and natural ferromagnetic minerals.

A ferromagnetic material acquires residual magnetization by fixing the magnetic moments, when it is cooled through the Curie temperature in a weak magnetic field. Such a remanent magnetization is the thermo-remanent magnetization (TRM). The author's experiment has shown that the fixing of magnetic moments can also be generated by volume development of ferromagnetic fine particles[1].

The specimen mentioned here is a Cu-Co alloy containing cobalt of about 2wt%. When the uniform solid solution of this alloy is kept at 750°C, the cobalt-rich ferromagnetic phase with f.c.c. structure is precipitated in the non-ferromagnetic matrix. It has been already established by many people[2] that the separation of two phases in the Cu-Co alloy is completed in the initial stage of aging and thereafter the average volume of precipitated Co particles increases by an aggregation process. In the aggregation process the total amount of the ferromagnetic phase is kept constant. In the present experiment the aging was made under the influence of a magnetic field the intensity of which is between 0.5 Oe and 500 Oe. The intensity of the total magnetization and the remanent magnetization was measured at various stages of aging by means of a high temperature ballistic method. Reversible magnetization was calculated as the difference between the total and remanent magnetization. Fig. 1 shows an example of these measurements. It is remarkable that the reversible magnetization rapidly increases in the first stage of aging, then the remanent magnetization arrives at its peak, and finally it gradually decreases to a small value.

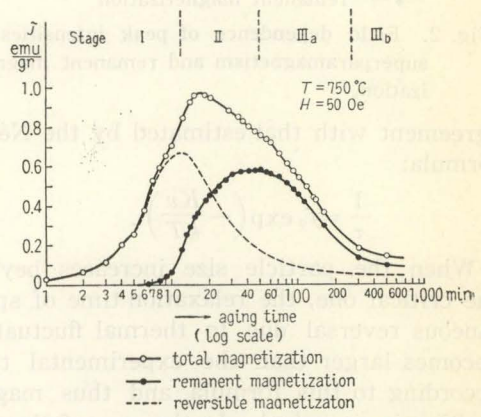

Fig. 1. Change in total, remanent and reversible magnetization of 2 wt % Co-Cu alloy as a function of aging time at 750°C in H_{ex}=50Oe.

Field dependence of peak values of the reversible and remanent magnetization obtained from the repeated measurements is shown in Fig. 2. The peak intensity of remanent magnetization approaches saturation in an applied field below 100 Oe, which is very weak compared with the coercive force of the material.

These results may be explained as fol-

lows: The precipitated particles are first superparamagnetic because of their very fine size. The average size at the peak of reversible magnetization was estimated to be roughly 100Å by the superparamagnetic granulometry method, i.e., by fitting the modified Langevin function[13] to the field dependence curve illustrated in Fig. 2. The size is in

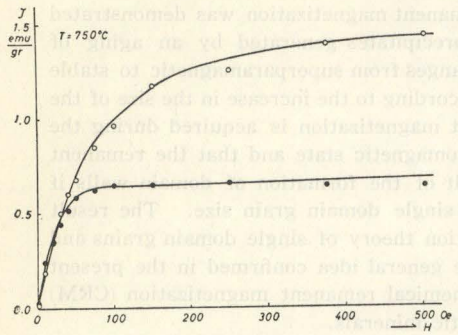

Fig. 2. Field dependence of peak intensities of superparamagnetism and remanent magnetization.

agreement with that estimated by the Néel's formula:

$$\frac{1}{\tau} = f_0 \exp\left(-\frac{Kv}{kT}\right).$$

When the particle size increases beyond the critical one, the relaxation time of spontaneous reversal due to thermal fluctuation becomes larger than the experimental time according to this formula and thus magnetization is quenched. In the case of thermoremanent magnetization, the quenching of magnetization is due to decrease in temperature and in this case it is due to increase in volume.

Another remarkable feature in the experiments was the decrease of the remanent magnetization in the later stage of aging. This fact can be interpreted in terms of the formation of reversely magnetized domains in the sufficiently developed particles of Co-rich precipitated phase.

This precipitation process is rather a simple one, but the phenomenon of the chemical remanent magnetization in synthetic and natural oxides may be also explained in the similar way.

Several specimens relevant to the chemical remanent magnetization are listed in the attached table. There seems to be a good correlation between the particle size shown in the 4-th column and the intensity and stability of remanence in the 2nd column. Such a correlation may be understood in terms of the nucleation process.

Considering the case of the reduction of α-Fe_2O_3 to Fe_3O_4, for example, a very small amount of Fe_3O_4 will be formed in the α-Fe_2O_3 grain. Accordingly as the chemical reaction proceeds, this nucleus will grow through each of the three stages of magnetic behaviour (i.e., superparamagnetic, stable single domain and multidomain) until the whole volume of the grain is completely filled with Fe_3O_4.

If the final size of the nucleus, developed in a magnetic field, is smaller than the critical size for a single domain grain, quenched magnetization will be observed as a chemical remanent magnetization. On the other hand, if the size is larger than the critical one, magnetization once quenched will decrease owing to the formation of reversely magnetized domains in the same nucleus.

In the extreme case where the nucleus grows to a considerably large size compared with the critical size, the chemical remanent magnetization will disappear so that the specimen will have only isothermal remanent magnetization in the applied field. Specimen No. 6 is an example of such a case.

In the above discussion magnetic interaction among the precipitates or between the precipitates and the matrix has been ignored. However, this problem of magnetic interaction may be important in relation to the self-reversal of the chemical remanent magnetization.

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Table I. Characteristics of several specimens relevant to CRM phenomena.

No.	Stage of nucleation	Stability and intensity of NRM or CRM	Ferromagnetic minerals concerned	Particle size of the minerals	Occurrence or method of production	Locality	Investigator	$J_n\left(\frac{\text{emu}}{\text{gr}}\right)$
1.	Superparamagnetic	No remanence	γ-Fe_2O_3		1. oxidation of $Fe(CO)_5$-vapour	Synthetic	Haul and Schoon[3] Knappwost[4]	0
				80～290Å (estimated)	2. dehydration of γ-FeOOH	Synthetic	Kobayashi[5]	0
2.	Nearly superparamagnetic	Unstable	α-Fe_2O_3	?	Soft component of NRM of Keuper Marls	Sidmouth (Britain)	Creer[6]	10^{-7}
3.	Magnetically-stable single domain	Stable and very large	γ-Fe_2O_3 (in a state of fine veinlets)	$<0.1\,\mu$	Weathered or altered rocks and iron ore deposits	Magnet Cove (U.S.A.), Kamaisi Obinata, Taisi, Kumano (Japan)	Kobayashi[7]	0.06～2.5
4.	Nearly single domain	Stable and relatively large	α-Fe_2O_3	$<0.1\,\mu$	1. red sandstone	Britain	Clegg, Almond and Stubbs[8] Creer[6]	10^{-7}～10^{-6}
					2. red shale	Japan	Nagata, Akimoto, Shimizu, Kobayashi and Kuno[9]	10^{-5}
5.	Transient from single domain to multidomain	Stable but relatively small	Fe_3O_4 γ-Fe_2O_3	0.1～0.6 μ	1. reduction of α-Fe_2O_3	Synthetic	Haigh[10] Kobayashi[7]	J_{cr}/J_{Tc}～1/10
					2. oxidation of Fe_3O_4	Synthetic	Kobayashi[7]	
6.	Perfectly developed multidomain	Unstable	Titano-maghemite	1～100 μ	Altered regions in dolerite sheet, andesite, etc.	Sidara basin, Central Japan	Akimoto and Kushiro[11]	10^{-5}
						Atumi, Northeastern Japan	Kobayashi and Kushiro[12]	10^{-5}

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DISCUSSION

E. THELLIER: How are the measurements made results of which are shown in Fig. 1? Is the field applied and removed alternately to measure total and remanent magnetizations ?

K. KOBAYASHI: Remanent magnetization shown in Fig. 1 was measured by switching off the electric current of the field coil for only several seconds. Except for the short intervals, constant magnetic field was applied through the whole stage of aging. The influence of the suppression of the applied field for such short intervals may be negligible in the magnetic results.

K. M. CREER: 1. How did you determine the grain sizes listed in your table ?
2. Have you assumed that the N.R.M. of the rocks listed is always wholly a C.R.M.? It may well be that the stable N.R.M. is partly due to the black ferromagnetic grains contained in rocks.

K. KOBAYASHI: 1. For superparamagnetic specimens (No. 1 in the table) I estimated the grain size by fitting the modified Langevin function to the field dependence curve. In other cases the determination of grain sizes was made by means of an electron microscope and an ore microscope.

2. Careful magnetic examinations have been made for the purpose of distinguishing the C.R.M. component from the whole amount of N.R.M. (*cf.* my article appeared in J. Geomag. Geoelect. Kyoto **10**, (1959) 99)

E. P. WOHLFARTH: The interactions may be assessed experimentally by determining the ratio of particle size obtained from magnetic measurements similar to those described (essentially "magnetic granulometry") to the size observed electron microscopically. The larger this ratio, the more important are the interactions. (See, for example, my paper, J. Electronics and Control, Jan. 1961)