

AGING TIME DEPENDENCE OF MAGNETIC HYSTERESIS PARAMETERS FOR Cu-Co SOLID SOLUTIONS

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This work gives the experimental results of H_c , H_R and I_R measurements as a function of aging time for Cu-1% Co solid solution aged at 600°C and 700°C.

On the basis of an analysis of the results there have been distinguished in the aging process: a superparamagnetic stage, stable single particles, stable agglomerations and multidomain particles or particles subject to incoherent rotation. Using the results of observations under an electron microscope and magnetic granulometry of the initial states we discuss the precipitation kinetics for long annealing times, and we assess the usefulness of the various granulometry techniques at different aging stages.

Introduction

It is well known that Co particles coagulated during aging in a homogeneous Cu—1% Co solid solution possess spontaneous magnetization approximately equal to that of the bulk material (Bean *et al.* 1959). Their magnetic behaviour depends on the uniformity of magnetization of the particle and its thermal agitation, both of these effects being strongly dependent upon the particle's volume. For a particle assembly we can investigate magnetic quantities as a function of particle volume by magnetic measurements on samples, the aging times of which are different.

Experimental procedure

a) The samples

The polycrystalline samples of Cu—0.9% Co and Cu—1.44% Co were obtained by powder metallurgy. The purity and percentage composition of the sample is shown in Table I.

After cold working of the ingot rod-shaped samples, 6 mm in diameter and 30 mm long, were prepared. The 0.9% Co sample had smaller grain than the 1.44% Co sample, as had been shown by a thermal micro-etching process during annealing. To make sure that there is a pronounced difference in grain size microphotographs of metallographic specimens were taken. The results are shown in Fig. 1.

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TABLE I

Spectrographic qualitative and polarographic quantitative analyses of samples. Czechoslovakian system of marking qualitative spectrographic results

Alloy	Trace elements																Co %					
	Ag	Pb	Cd	Bi	As	Sb	Sn	Ge	W	Au	Al	Zn	Co	Ni	Ta	Ti		Fe	Ba	Mg	Si	Te
	Detectability in %																					
	10 ⁻³	10 ⁻³	10 ⁻³	10 ⁻³	10 ⁻²	10 ⁻²	10 ⁻³	10 ⁻³	10 ⁻²	10 ⁻²	10 ⁻³	10 ⁻²	10 ⁻²	10 ⁻²	10 ⁻²	3 × 10 ⁻³	10 ⁻²	3 × 10 ⁻²	3 × 10 ⁻⁴	10 ⁻³	10 ⁻²	
Cu-Co 1%	0	2	1	4	—	2	—	—	2	—	—	?	p	—	?	—	?	1	—	2	—	1.44
Cu-Co 1%	—	—	?	3	—	—	?	—	—	—	—	—	p	3	—	?	—	—	2	2	—	0.9

Symbol: “—” — no line of a given element, ? — uncertain presence or absence of an element, o — barely visible line, 1 — very weak line, 2 — weak line, 3 — strong line, 4 — very strong line

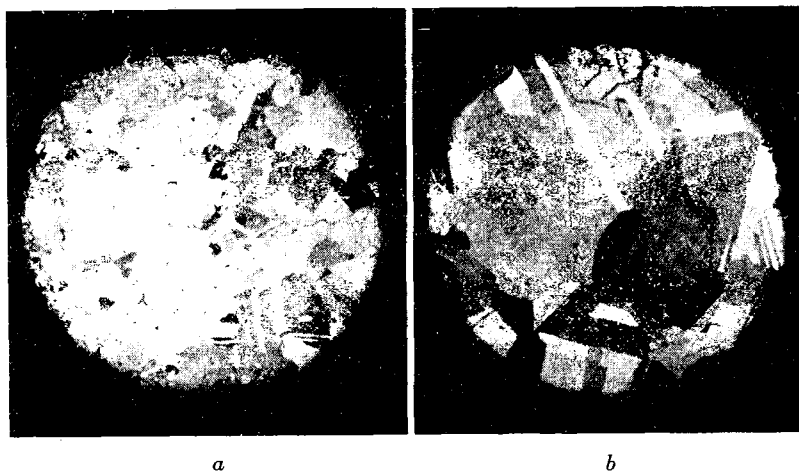


Fig. 1. Microphotographs of metallographic specimens (100 \times). *a* — 0.9% Co sample, *b* — 1.44% Co sample

The samples were solution treated at 1020°C and, after rapid cooling, aged isothermally at 600°C and 700°C. The precipitation process was controlled by choosing different times of the isothermal heat treatment.

b) Measurement techniques

The saturation magnetization was found by extrapolation from a plot of magnetization versus H^{-1} . Magnetization in high fields (of the order of 10^4 oersteds) was measured in an electromagnet by the ballistic method. The coercive force H_c , remanence coercive force H_R , and the remanence I_R , were measured by a Neumann coercive force-meter manufactured by the Institute of Iron Metallurgy in Gliwice (Stryk 1962).

The remanence coercive force H_R , is the field which reduces to zero the magnetic remanence. It was found by extrapolation of I_D versus H_D curves to zero, where I_D is the magnetic remanence obtained after application and reduction to nil the field H_D in the direction opposite to I_R . The details of the method applied will be published elsewhere (Figiel *et al.* 1968).

Results and discussion

a) Aging time dependence of H_c , H_R and I_R

Figures 2, 3 and 4 present H_c , H_R and I_R as a function of aging time t for the 0.9% Co and 1.44% Co samples treated at 600°C and for the 1.44% Co sample treated at 700°C.

The anomalies at the initial part of the curves can be seen. They consist in the appearance of a sharp maximum of the ratio H_R/H_c in the initial states of precipitation. Bate *et al.* (1955) have observed a similar anomaly for Cu—Co and Cu—Fe solid solutions and they believed this to be due to the reduction of stresses during the aging process.

It seems more probable that this anomalous behaviour can be explained by the differences in the volumes of the precipitated particles. At first, large agglomerations of cobalt of

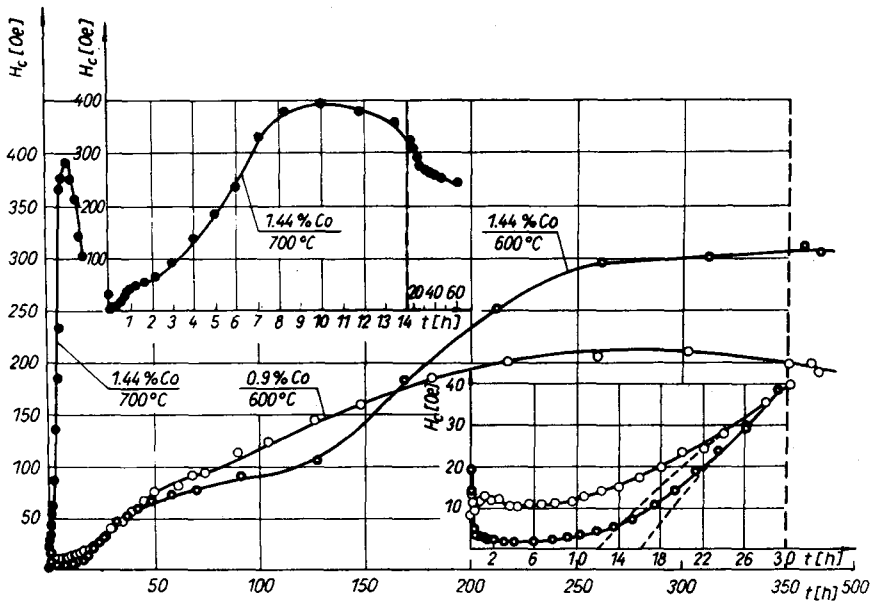


Fig. 2. H_c versus t for 1.44% Co and 0.9% Co samples

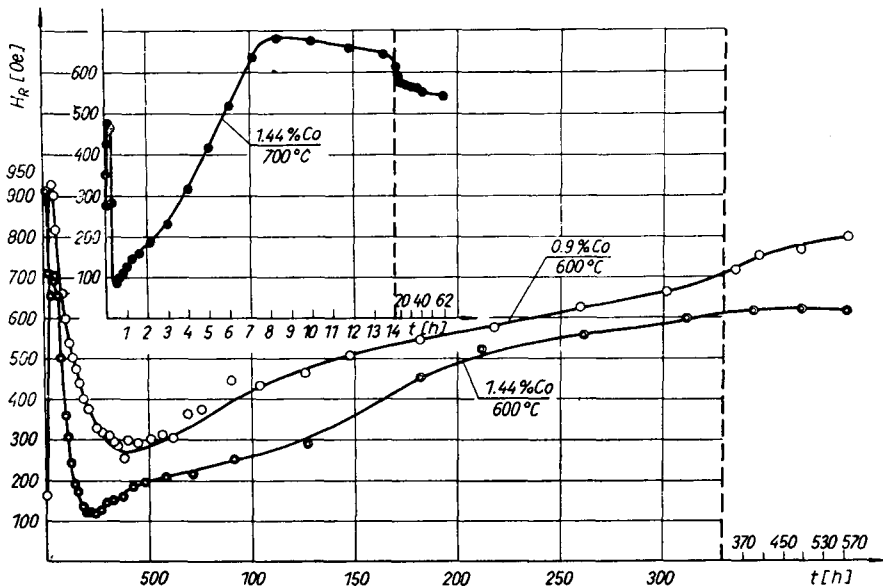


Fig. 3. H_R versus t for 1.44% Co and 0.9% Co samples

a stable magnetic moment arise on the lattice imperfections during supersaturation and they grow rapidly with longer annealing. They give a large H_R which becomes larger with longer times of annealing (H_R depends on the properties of the magnetically stable phase only). The total quantity of precipitated cobalt is very small, however, as is indicated by the very

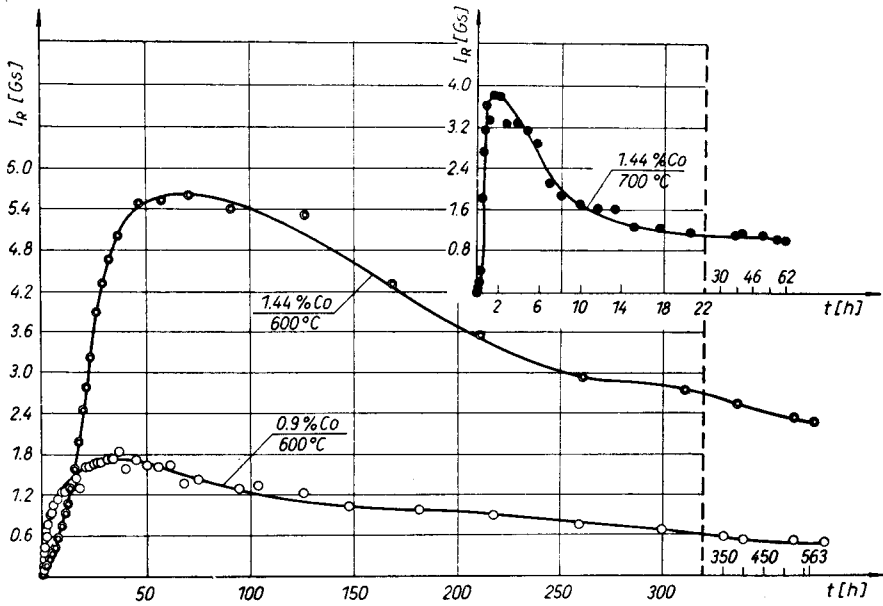


Fig. 4. I_R versus t for 1.44% Co and 0.9% Co samples

small value of I_R (e.g., 1.2×10^{-3} gauss for the 1.44% Co sample). The coercive force is rather small owing to the homogeneous precipitation (already during rapid quenching) of a large number of small, hence unstable, particles which easily screen the magnetic moment of a minute stable phase while measuring $H_c \cdot H_c$ is decreased at the initial aging stages owing to the further precipitation of this unstable phase. H_R begins to drop only when these homogeneously precipitated particles begin to grow, thanks to diffusion, forming stable particles. These particles are smaller and easier to reverse magnetically than these precipitated during quenching.

Gerlach (1949) devised a simple version of a model giving a low value of H_c , in which he divided all particles into two groups of intrinsic coercive forces H_{c1} and H_{c2} . If in the mixture the particles with H_{c1} have a concentration c_1 and $H_{c1} \ll H_{c2}$, then the resultant coercive force rapidly drops to H_{c1} if c_1 increases.

The results of the works by Becker (1957) and Sato and Mitui (1964) do not show the anomaly described above. These authors measured the coercive force by the ballistic technique and in this case one may expect a decidedly lesser sensitivity than that of the Neumann coercive force meter with an internal permalloy probe.

A comparison of the curves in Figs 2, 3 and 4 indicates that the samples pass through the same characteristic stages during aging. It may be conjectured, therefore, that the character of the precipitation process remains unchanged with the aging temperature and with the grain size of the sample; only the kinetics of the process changes. One can see that for the times of 12 hours (0.9% Co sample), 16 hours (1.44% Co sample treated at 600°C) and 1.2 hours (1.44% Co sample treated at 700°C) the coercive force shows points of inflection. Moreover, we see that the I_R/I_S ratio does not attain its theoretical maximum

value (it reaches 0.26, 0.34 and 0.34 for the samples in the above succession), as it becomes stable much quicker than the coercive force, according to Fig. 5 showing I_R/I_S as a function of aging time, t . The times in which this maximum is reached are 35 hours, 70 hours and 1.66 hours, respectively. This points to a possible cause of these phenomena, *viz.* that at this stage of aging the precipitated particles begin to form agglomerations. Because of this (the formation of agglomerations with zero remanence) the remanence drops and the coercive force rises slower than initially.

The division of the aging process into stages is visualized in Fig. 6 which shows H_c versus I_R for the three tested samples. We see that for times of 300 hours, 385 hours and 10 hours the coercive force achieves maximum values. The continued decrease is associated

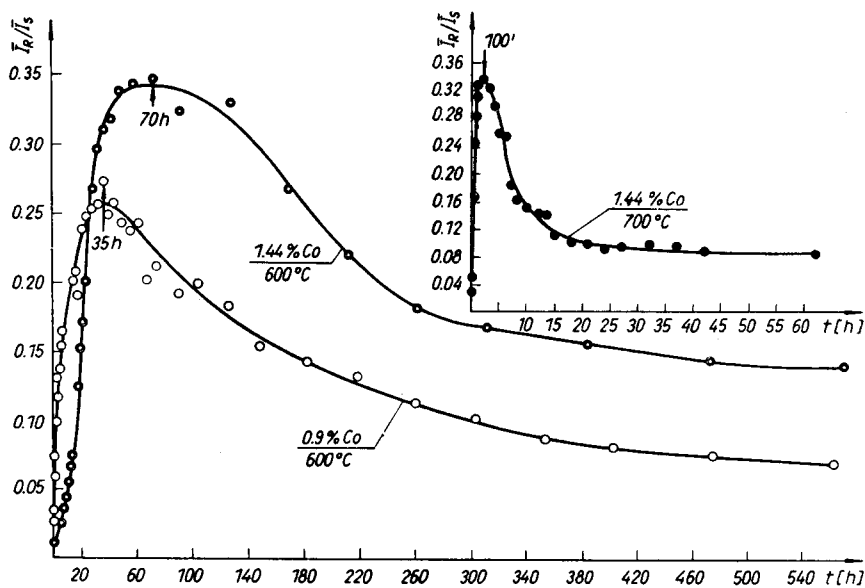


Fig. 5. I_R/I_S versus t for 1.44% Co and 0.9% Co samples

with the transition of single-domain particles into multidomain particles, or with single-domain particles whose magnetization undergoes incoherent rotation in the magnetic field.

As the beginning of the first stage of aging (growth of stable single-domain particles) we assume the aging time at which $H_c \approx 0$ according to the extrapolation as in Fig. 2, which gives the respective times equal to 12 hours, 16 hours and 0.4 hour for 0.9% Co (600°C), 1.44% Co (600°C) and 1.44% Co (700°C) samples, respectively.

Comparing the times for zero, inflection and maximum H_c , and also from the maximum of I_R/I_S we see that with an increase of the aging temperature by 100°C the processes occur faster by an average of 43.6 times (for the 1.44% Co sample). We also see that the kinetics of precipitation changes with the grain size. The 0.9% Co sample of smaller grain has a higher precipitation rate, which is in qualitative agreement with the results of the work by Raadschelders (1966).

Interesting information is obtained by comparing the maximum values of the coercive force. The theoretical maximum of coercive force for stable cobalt particles of cubic anisotropy ($K_1 < 0$) and randomly oriented easy axes is 430 oersteds at room temperature, $K/I_s^2 = 678$ oersteds, measured by Bean *et al.* (1959). The observed maxima of H_c are 210 oersteds, 310 oersteds and 390 oersteds, respectively. It is seen that the measured

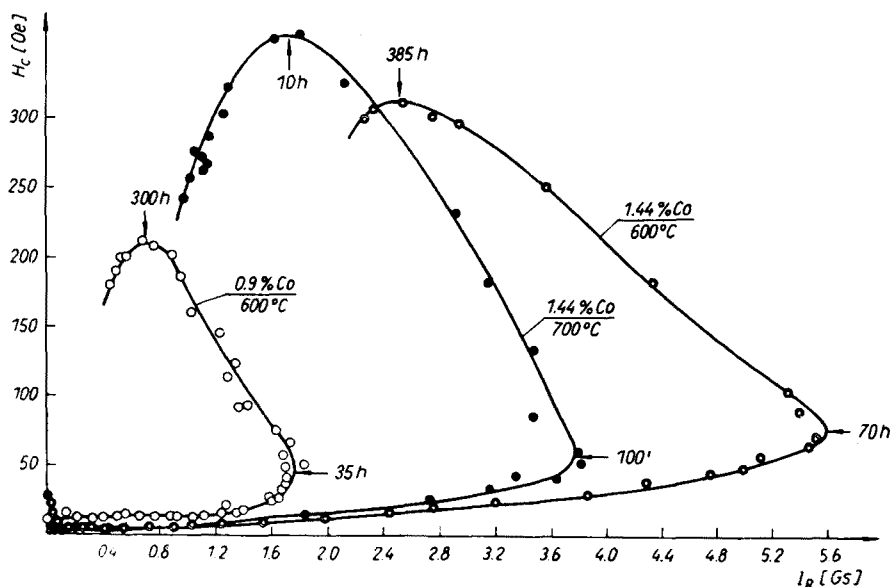


Fig. 6. H_c versus I_R for 1.44% Co and 0.9% Co samples

values decrease with aging temperatures, and also with smaller grain size of the crystallites. Both these factors give preference to heterogeneous precipitation (*i.e.*, precipitation on lattice imperfections). The small coercive force of heterogeneously precipitated cobalt particles is due either to the formation of zero remanence agglomerations or to the incoherent rotation of magnetization vectors.

b) Particle coarsening and comparison of different granulometric methods

By assuming $V = \alpha \cdot t$, and inserting this into the formula derived by Bean and Livingston (1959), one can get for the coercive force as a function of aging time (t) the expression

$$H_c = A - Bt^{-\frac{1}{2}}$$

where $A = 0.64 K/I_s$,

$$B = 3.2/I_s(KkT/\alpha)^{\frac{1}{2}},$$

V — is the particle volume,

I_s — the saturation magnetization of the particle,

K — the magnetic anisotropy constant,

k — the Boltzmann constant,

T — the temperature of measurement

and α — is the constant rate of particle coarsening which depends on the temperature of aging, the concentration of cobalt and on the grain size of the sample.

If the assumed theoretical model is correct, then the plot of H_c against $t^{-\frac{1}{2}}$ should be a straight line. The experimental curves of these dependences are given in Figs 7, 8 and 9. One can see that in all of these cases, including the results of Sato and Mitui (1964), none of

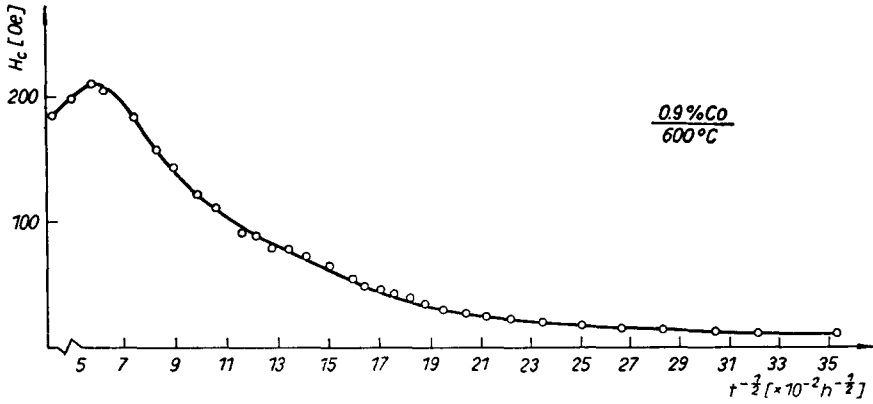


Fig. 7. H_c versus $t^{-\frac{1}{2}}$ for 0.9% Co sample aged at 600 °C

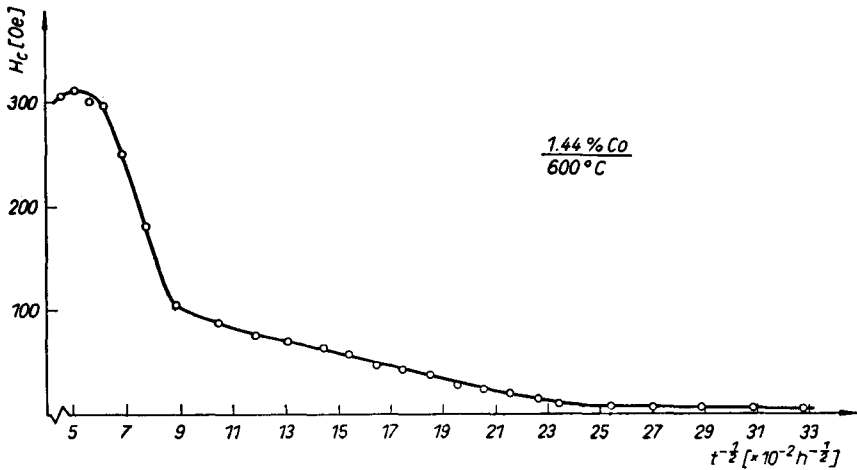


Fig. 8. H versus $t^{-\frac{1}{2}}$ for 1.44% Co sample aged at 600 °C

these plots represent a straight line. This proves that Bean's model is oversimplified, but this does not contradict the assumed precipitation kinetics as we shall see later.

Let us maintain the assumption that the mean volume of the particles increases linearly with the annealing time (even for long times t). The coefficient α can be determined from measurements of \bar{V} for the initial annealing states. \bar{V} has been calculated from the slope of the \bar{I} versus H^{-1} curve at $H \rightarrow \infty$ according to a method proposed by Cahn (1957). The experimental results (Krop and Mizia 1968) give $\alpha_e = 8 \times 10^{-20}$ cm³/h for the 1.44% Co

sample, and $\alpha_e = 13 \times 10^{-20}$ cm³/h for the 0.9% Co sample. For annealing at 700°C the value of α_e was estimated by multiplying $\alpha_e = 8 \times 10^{-20}$ cm³/h by 43.6. Table I contains the volumes calculated as $V = \alpha_e \cdot t$ and their corresponding radii for different t and, in addition, it also gives in column 4 the values of \bar{V} for different t 's determined by direct observations under an electron microscope (Krop *et al.* 1967) for the 1.44% Co sample annealed at 600°C.

By extrapolation of the H_c versus t curve to zero (Fig. 2) we have determined the times of formation of magnetically stable particles. The volumes corresponding to these times

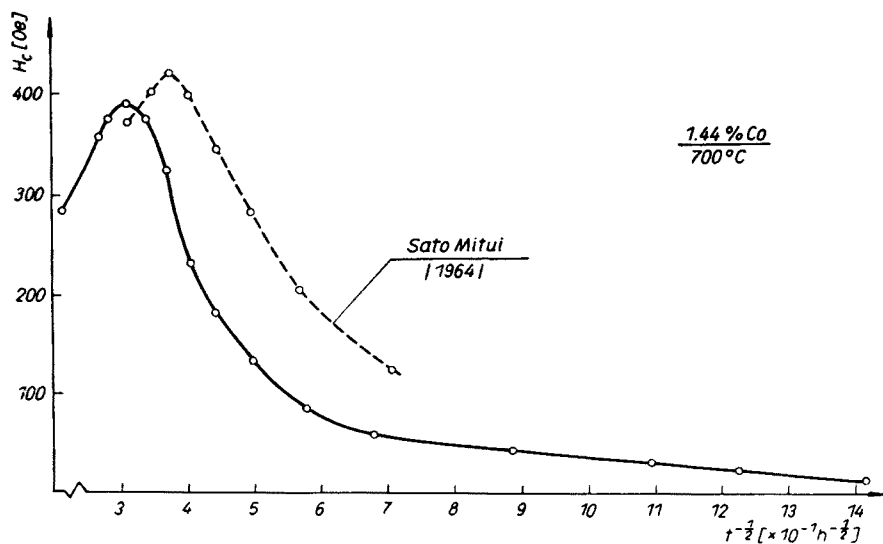


Fig. 9. H_c versus $t^{-1/2}$ for 1.44% Co sample aged at 700°C. Dashed curve H_c versus $t^{-1/2}$ for 2% Co sample aged at 700°C, by Sato and Mitui (1964)

(denoted by the asterisk in the table) are, as can be seen, approximately in agreement with one another and with the theoretical value $V_s = 25 kT/K \approx 1.08 \times 10^{-18}$ cm³ (the anisotropy constant was taken from Bean *et al.* 1959).

Another confirmation of the assumption of the proportional rise in volume with time is the conformity of the volume determined magnetically (as $V = \alpha_e \cdot t$) with that determined by means of the electron microscope for the time of 24 hours and the 1.44% Co sample. For this time the precipitated particles gave very distinct contrast (Krop *et al.* 1967, Fig. 2) and the statistics comprised 617 particles. In this case we obtained conformity of the radii of the spherical precipitates within the limits of ± 1.5 per cent. For short annealing times (1.66 and 6 hours), owing to the fact that the electron microscope "does not see" small particles, the mean volume is calculated from the "totalized" distribution, which gives considerable overrating of its value (Table I) and at the same time underrates the packing fraction (Krop *et al.* 1967). As regards the result after 100 hours of annealing, the large statistical error (the photograph only gave a statistics of 130 particles) does not permit us to completely rely on the determined mean value.

TABLE II

Aging time dependence of \bar{V} and corresponding r estimated as $\bar{V} = \alpha_c \cdot t$ and by electron microscopy (second column) for different samples and aging temperatures

Aging time t [h]	$\bar{V} \times 10^{-18} \text{ cm}^3$ 1.44% Co, 600°C $\alpha_c = 8 \times 10^{-20} \text{ cm}^3/\text{h}$	$r = (3\bar{V}/4\pi)^{1/3}$ [Å]	$\bar{V} \times 10^{-18} \text{ cm}^3$ 1.44% Co, 600°C electron microscope	r [Å]	$\bar{V} \times 10^{-18} \text{ cm}^3$ 1.44% Co, 700°C $\alpha_c = 3.48 \times 10^{-18} \text{ cm}^3/\text{h}$	$r = (3\bar{V}/4\pi)^{1/3}$ [Å]	$\bar{V} \times 10^{-18} \text{ cm}^3$ 0.9% Co, 600°C $\alpha_c = 13 \times 10^{-20} \text{ cm}^3/\text{h}$	$r = (3\bar{V}/4\pi)^{1/3}$ [Å]
0.4								
1.66	0.1333	31.7	0.667	54.3	1.39*	69.4*		
6	0.48	48.5	1.37	68.8				
10					34.8**	202.7**		
12							1.56*	71.9*
16	1.28*	67.6*	2.12	79				
24	1.92	76.8	13.9	149				
100	8	124						
300								
400	32 **	197 **					39**	210**

* — mean volumes and radii for aging times determined from extrapolations of H_c versus t curve to zero,
 ** — mean volumes and radii for aging times corresponding to the maximum of H_c .

Yet one more confirmation of the correctness of the assumption of proportional growth of volume with annealing time is the approximate conformity between the volumes determined as $\alpha_e \cdot t_e$, where t_e is the time corresponding to the maximum of H_e (these volumes are marked by the double asterisk in the table). On the basis of these volumes we computed the mean critical radius of the particle corresponding to the maximum coercive force, and found it to be equal to approx. 200 Å. This radius can be assessed from the theory of incoherent rotation (*cf.* Brown 1963, p. 79) to be equal to about 105 Å for a spherical particle, with the constant $C = 2.06 \times 10^{-6}$ ergs/cm (*i.e.*, for pure hexagonal cobalt). The result obtained on the basis of the considerations of Kondorski (1952) is about 250 Å. It is larger because the author takes the state of incoherent magnetization distribution in the particle to be stable and not intermediate. These theoretical deliberations are just a rough estimation, as neither the particle shape for long aging times nor the value of C for cubic cobalt in a copper matrix are known.

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