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Mechanical and magnetic hardening in CuNiCo alloy

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A study of mechanical and magnetic hardening in the CuNiCo alloy has shown that two distinct mechanisms are responsible for two types of hardening. The mechanical hardening of the alloy, which occurs after a short ageing time is due, according to Cahn's theory, to the mechanical stresses induced by the spinodal decomposition of the supersaturated solid solution. Magnetic hardening, which occurs much later than mechanical hardening, is due to the appearance of the ferromagnetic γ_1-phase, which reaches single domain particle size during a discontinuous transformation process by volume growth and segregation between the γ_1- and γ_2-phases.

1. Introduction

The magnetic properties of the magnetically hard CuNiCo alloy are determined mainly by the ferromagnetic phase size and by the chemical constitution of the phases which appear during spinodal decomposition of the supersaturated solid solution [1]. The phase transformation in this system may be written

$$\gamma_{\mathrm{fcc}} \rightarrow \underset{\substack{\text{coherent f c c}}}{[\gamma_1+\gamma_2]'} \rightarrow \underset{\substack{\text{tetragonal}\\ \text{partial}\\ \text{coherency}}}{[\gamma_1+\gamma_2]'} \rightarrow \underset{\substack{\text{cubic}\\ \text{partial}\\ \text{coherency}}}{[\gamma_1+\gamma_2]_{\text{equil.}}} \quad (1)$$

The decomposition products are parallel to the $\{1\,0\,0\}$ matrix surface and in the final state, in the late ageing stages, the γ_1-phase is NiCo-rich and the γ_2-phase is Cu-rich. In the alloy with optimum magnetic properties the ferromagnetic γ_1-phase particles are close to the critical size required to be single domains.

Joffe and Gaunt [2] investigated thermal dependence of the coercivity over the temperature range 77 to 300 K for the $Cu_{49.28}Ni_{21.64}Co_{29.8}$ alloy aged at 973 K for 5 to 1000 min. The results obtained seem to suggest that the magnetic hardening of the alloy is due to the ferromagnetic phase shape anisotropy and to change in volume of this phase during ageing. The dependence of the magnetic hardening in the early stages of the ageing process on the heat-treatment temperature has not so far been investigated; the mechanical hardness of CuNiCo has also not been studied. Such investigations may supply additional information about the alloy structure changes. It should be emphasized that the ageing treatments of the CuNiCo alloy produce a heterogeneous two-phase structure and that the mechanical and magnetic hardness depend on the nature of the segregation at a particular ageing time.

The purpose of this work was to explain magnetic and mechanical hardening processes of the magnetically hard CuNiCo alloy.

2. Experimental procedure

The investigation was carried out on CuNiCo alloy which was alloyed and cast in vacuum. Its chemical composition was: 49.79 wt% Cu, 20.84 wt% Ni, 29.35 wt% Co.

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The samples investigated were disc-shaped, 3 mm thick and 20 mm in diameter. In order to eliminate dendritic segregation all the samples were first homogenized by heat treatment for 50 h at 1370 K in pure hydrogen and then quenched in an ice–water mixture. Further thermal ageing of the alloy was carried out in molten salt baths at 870, 910, 950, 990 and 1030 K for different periods of time varying from 5 to 10 800 sec. The ageing temperature was controlled to ± 3 K. After each treatment, the samples were again quenched in an ice–water mixture.

Vickers hardness measurements were taken on each sample with a minimum of ten readings per sample.

The magnetic hardness was defined by coercivity measurements, carried out at room temperature by means of the Förster coercivity meter with an accuracy of the order of 1%.

3. Results and discussion

The hardness and coercivity isotherms obtained are shown in Figs 1 and 2, respectively.

Comparison of the curves in Fig. 1, which are typical for the precipitation hardening systems, shows that the hardness reaches a maximum after about 15 sec for each ageing temperature. The absolute value of the maximum hardness also increases as the reaction temperature decreases.

From the curves in Fig. 2, where the results of Joffe and Gaunt [2] are plotted, it can be seen that the magnetic hardening of the alloy takes place much later than the mechanical hardening. For all the isothermal annealing temperatures, in the range examined, the coercive force increases with ageing time although no perceptible increase can be observed until the alloy has been heat treated for at least 60 sec. The maximum in the isotherms can be expected (except for 990 and 1030 K) after ageing times much longer than those used in this work. As in the case of mechanical hardening the absolute maximum in the coercive force apparently increases as the temperature of the transformation decreases.

The changes of hardness observed with the temperature and the annealing time can be explained in the case of the mechanical hardness by means of Cahn's theory of spinodal decomposition [3, 4], and in the case of the magnetic hardness by the single domain particle theory of permanent magnets.

The critical shear stress, τ_c, for the modulated structure created in the spinodal decomposition can be expressed according to Cahn's theory

$$\tau_c = 0.57(A\eta Y)^3\left(\frac{\gamma\beta}{\mathbf{b}}\right)^{2/3}. \qquad (2)$$

In this experiment A is the amplitude of the compositional fluctuation and is given by $A = C - C_0$ (the difference between the actual concentration C and the average concentration C_0), η is a parameter describing the compositional dependence of the lattice parameter, γ is the self energy of the dislocation, β is $2\pi/\lambda$ (where λ is the wavelength of the compositional fluctuations), $\mathbf{b}$ is the Burger's vector and $Y = (c_{11} + 2c_{12})(c_{11} - c_{12})/c_{11}$ (where c_{ij} are the coefficients of elasticity).

The spinodal transformation occurring in the early stages of ageing causes the sudden chemical

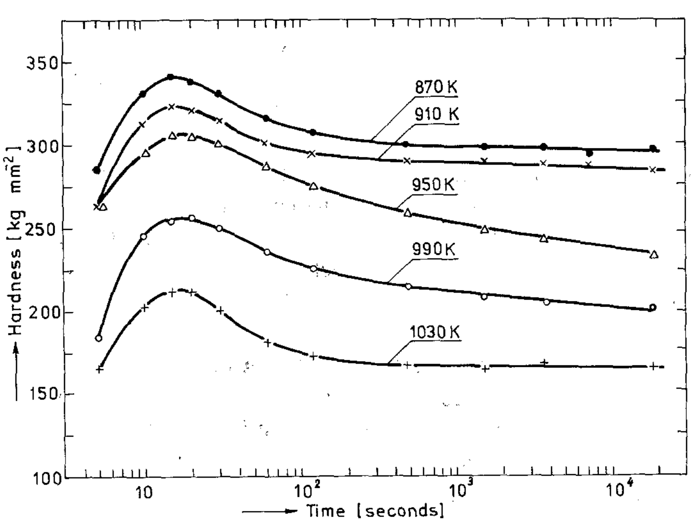

Figure 1 Hardness isotherms of the CuNiCo alloy.

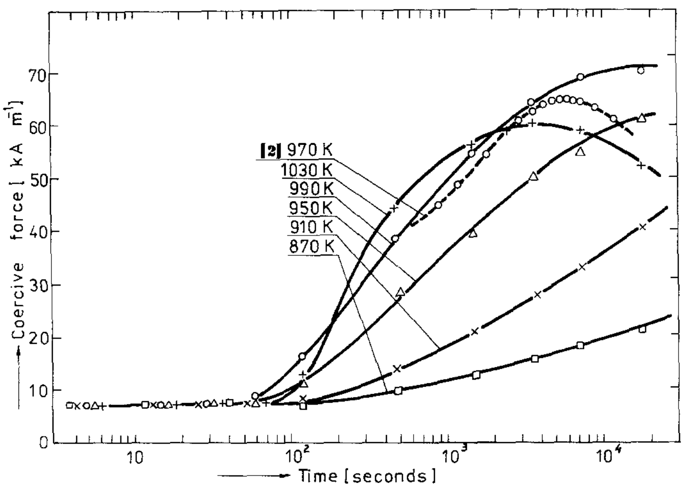

Figure 2 Coercive force isotherms of CuNiCo alloy.

composition change within the whole sample volume, and the modulation wavelength changes with the ageing time. So, according to Equation 2 it can be assumed that the modulation wavelength increases during the period in which the mechanical hardness is increasing. Such an interpretation has also been proposed by Butler and Thomas [5] who found that very rapid changes in the chemical composition occurred within 1 min at 898 K. An 82% compositional change occurred during this period but only over regions about 2 to 3 nm in width.

The mechanical hardness maximum dependence on the ageing temperature can be understood if it is assumed that the amplitude $A = C - C_0$ increases with decreasing temperature.

The magnetic properties of magnetically hard materials such as CuNiCo can be "explained" in terms of the Stoner–Wohlfarth [6] theory of hysteresis in heterogeneous alloys containing non-interacting elongated single domain particles with uniaxial shape and anisotropy. In terms of that theory the coercive force H_c is described by the equation

$$H_c = p(1-p)(N_b - N_a)(I_{s1} - I_{s2})^2/I_s, \quad (3)$$

where p is the filling coefficient of the ferromagnetic γ_1-phase with I_{s1} magnetization; I_{s2} is the magnetization of the weakly magnetic γ_2-phase; I_s is the alloy magnetization; N_a and N_b are the transverse and longitudinal demagnitization coefficients of the ellipsoid.

Equation 3 shows that the value of the coercive force depends on the magnetization, packing density and dimensional ratio (which determines the values of N_a and N_b) of the stable ferromagnetic phase.

The spinodal transformation does not cause the decomposition of the CuNiCo alloy to stable γ_1- and γ_2-phases, but only a structural modulation of the composition which is subsequently absorbed in the course of the discontinuous transformations. During that last transformation, volumetric growth of the ferromagnetic γ_1-phase precipitations takes place almost uniformly within the whole volume of the alloy. The volumetric growth of the γ_1-phase precipitations, whose final shape should depend on the coherency with the matrix and the anisotropy of stresses throughout the alloy will proceed, as stated by Joffe and Gaunt [2], until there is loss of coherency between the ferromagnetic γ_1-phase and the paramagnetic γ_2-phase. Such an interpretation is supported by the fact that coercive force changes appear after a definite ageing period (see Fig. 2), during which the γ_1-phase particles reach a size close to the critical size. This agrees with the conclusions reached by Kneller and Luborsky [7] who found that the increase in coercivity occurs when the precipitated particles reach the critical size, about 30 nm.

Simultaneously, with the particle size during ageing, the further diffusion segregation of elements between phases continues which causes an increase in the saturation magnetization difference between the phases. Finally, the temperature dependence of the maximum coercive force can be related to the difference in composition between the precipitates and the matrix. Taking into consideration that, to a first approximation, the coercive force is proportional to the magnetization difference between the phases (see Equation 3), and therefore to the chemical composition difference, it can be expected that the coercive force should increase as the temperature of the spinodal decomposition decreases.

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