QUALITY INSPECTION OF SINTERED POWDER TUNGSTEN-COBALT PRODUCTS BY MAGNETIC TECHNIQUE

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Abstract: The physical structure of sintered powder W-Co alloys consists of hard non-magnetic particles of tungsten carbide cemented by plastic interlayers of cobalt, which is ferromagnetic. Strength characteristics and magnetic parameters are governed mainly by the composition and the structural state of the cobalt binder, which provides a tool for magnetic inspection of the quality of sintering.

Introduction: Hard tungsten-cobalt alloys produced by powder metallurgy consist of nonmagnetic grains of tungsten carbide bound by cobalt interlayers. The strength properties of these alloys are largely governed by the mean thickness and the structural state of the cobalt interlayer. Since cobalt is a ferromagnet, the alloys also display magnetic properties despite a considerable content of the non-ferromagnetic WC-phase. The magnetic characteristics of the alloys are closely associated with the structural parameters of the cobalt interlayer, and this is what enables magnetic technique to be used for the nondestructive quality inspection of sintered hard-alloy products. For instance, magnetic methods can be used to control the mean size of the grains of tungsten carbide and carbon content in the cobalt interlayer after sintering.

The coercive force H_C is the structure-sensitive magnetic characteristic of hard alloys. Despite numerous works on establishing relations between the coercive force and the structural state [1 – 4], the mechanism of H_C forming in hard alloys has not been completely clarified. Attempts to use Kersten's theory of "inclusions" [5] to explain the growth of H_C in hard alloys as the content of the non-magnetic carbide phase (WC-phase) grows lead to considerable discordance between the numerical evaluation and experimentally observed values of H_C [1]. This is explicable, for in hard alloys, with 90 or more volume percent of the non-magnetic phase of tungsten carbide, the mechanism of interaction between the domain walls and non-magnetic inclusions by Kersten's model becomes impossible.

In [6] an empirical formula relating the coercive force of hard alloys to the mean size of tungsten carbide grains $\langle D\rangle$ was obtained,

$$H_C = 135 / \langle D\rangle. \qquad (1)$$

However, eqn (1) did not take into account cobalt content which had a considerable effect on the coercive force of the alloys – H_C decreased as cobalt content increased. Cobalt content can be taken into account if the mean thickness of the cobalt interlayer $\langle h\rangle$ is used in the calculations. If the cobalt content and the mean size of carbide grains in a hard alloy are known, the mean thickness of the cobalt interlayer can be evaluated.

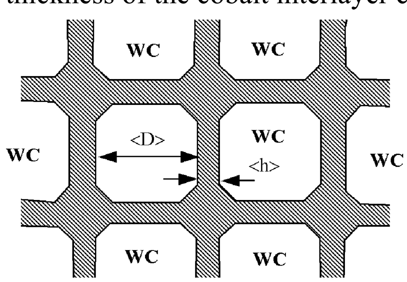


Fig.1. A model of the structure of hard alloys

Assuming that the carbide grains are cubic and that they are surrounded by a cobalt interlayer (fig.1), we arrive at the following mean value of the cobalt interlayer thickness: of the cobalt interlayer can be evaluated. Assuming that the carbide grains are cubic and that they are surrounded by a cobalt interlayer (fig.1), we arrive at the following mean value of the cobalt interlayer thickness:

$$\langle h\rangle = \langle D\rangle \rho_{WC} C_{Co} / \rho_{Co}(1 - C_{Co}), \qquad (2)$$

where ρ_{WC} and ρ_{Co} are the densities of tungsten carbide and cobalt respectively; C_{Co} is cobalt mass fraction.

It is considered in this case that the cobalt interlayer has a small thickness h and that it is solid and continuous.The introduction of $\langle h\rangle$ enables one to characterize the structure of alloys with different carbide grain sizes and different cobalt contents by one parameter – the mean thickness of the cobalt interlayer.

Results: In the case of a thin cobalt interlayer, the reversal of magnetization and the nature of hysteresis in hard alloys may be treated the same way as in the case of thin magnetic films. For thin ($h < L$, where L is domain size) ferromagnetic films containing Bloch walls, the magnetostatic energy of the magnetic pole leakage fields appearing at the intersection of the domain walls and the film surface becomes comparable with the anisotropy energy and the exchange energy, consequently,it cannot be neglected, as distinct from the case of massive materials.In [7] the magnetostatic energy E_M of a Bloch domain wall in a thin film was calculated with the approximation of the wall by an elliptic cylinder, as shown in fig. 2 as follows:

$$E_M = 2\pi M_B^2\, \delta/(h+\delta), \qquad (3)$$

where M_B is effective magnetization of the Bloch wall along the normal to the film surface, δ is domain wall thickness. Then, taking into account that $M_B \approx M_S/\sqrt{2}$ when $h < \delta$, the surface density of the energy of a Bloch wall can be written as

$$\gamma = \pi^2 A/\delta + \delta K/2 + \pi\delta^2 M_S^2/(h+\delta), \qquad (4)$$

where A is an exchange parameter, K is an effective constant of magnetic anisotropy, M_S is saturation magnetization. It follows from eqn (4) that the energy of domain walls (and hence the coercive force) depends on film thickness h as well.

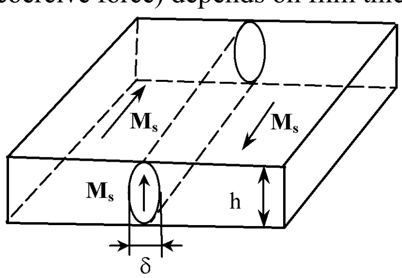


Fig.2. A model of the Bloch wall in a thin magnetic film

According to [7], the expression for the coercive force governed by the variations in the thickness of the magnetic film has the form

$$H_C^h = 4{,}2(A^2/M_S)\langle h\rangle^{-4/3}(dh/dx), \qquad (5)$$

where dh/dx is the gradient of the thickness of the cobalt interlayer in the direction of the moving domain wall. Equation (5) is true for $L > h > \delta$ where δ is domain wall thickness and L is domain size. Besides, domain walls, when moving, interact with various defects of the crystalline structure, nonmagnetic inclusions etc, thus inducing hysteresis H_C^d stemming from the structural state of the film. Then the coercive force of hard alloys is described by the expression

$$H_C = H_C^d + 4{,}2(A^2/M_S)\langle h\rangle^{-4/3}(dh/dx)\,. \qquad (6)$$

As a domain wall moves, the greatest gradient the cobalt interlayer thickness falls on the intergranular regions and it is largely determined by the shape of carbide grains. Since experiments show that the shape of tungsten carbide grains practically remains unchanged on powder crushing, it can be considered in the first approximation that $dh/dx = \text{const}$. Then eqn (6) can be reduced to the form

$$H_C = a + b\langle h\rangle^{-4/3}, \qquad (7)$$

where *a* and *b* are constants found from the dependences $H_C = f(\langle h\rangle)^{-4/3}$ constructed by experimental data for alloys with different mean cobalt interlayer thicknesses, $\langle h\rangle$ being calculated by eqn (2). Fig.3 shows that the experimental values of H_C for alloys with different cobalt contents and different carbide grain sizes lie satisfactorily on a straight line.

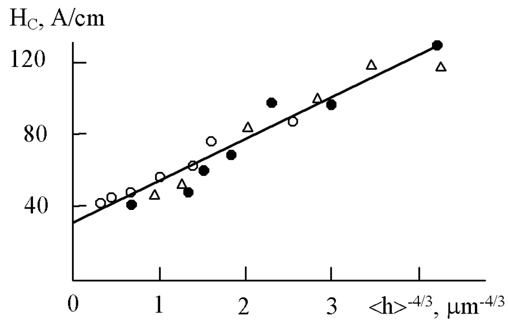


Fig.3. A correlation between H_C and $\langle h\rangle^{-4/3}$ for some hard alloy

The length *a* cut off by the straight line $H_C = f(\langle h\rangle)^{-4/3}$ on the ordinate axis determines H_C^d – the hysteresis of the cobalt interlayer stemming from its structural state (the density of the crystalline structure, inclusions, the number of tungsten and carbon atoms dissolved in the cobalt phase, the magnitude of internal and external elastic stresses). It follows from fig.3 that $H_C^d \approx 30$ A/cm. Note that, though H_C^d depends on the structural state of the cobalt interlayer, it is approximately constant for different alloys.
The coefficient *b* is found by the tangent of the slope of the straight line $H_C = f(\langle h\rangle)^{-4/3}$.

Then the expression for the coercive force of hard alloys fabricated under laboratory conditions (the narrow fraction of the carbide grain size) can be

$H_C = 30{,}2 + 21{,}7\langle h\rangle^{-4/3}$ (A/cm), (8)

where <h> is the mean thickness of the cobalt interlayer, or, in view of eqn (2),

$H_C = H_C^d + H_C^h = 30{,}2 + 21{,}7[(\langle D\rangle \rho_{WC} C_{Co} / \rho_{Co} (1 - C_{Co})]^{-4/3}$ (A/cm). (9)

The values of <D> and <h> are given in micrometers.

Discussion: Figs. 4 and 5 present data on the measured coercive force of alloys with different cobalt contents and different carbide grain sizes. Dashed are curves predicted by eqn (9). The value of H_C is seen to increase as cobalt content and the carbide grain size decrease, since in either case the thickness of the cobalt interlayer decreases. It is also obvious that the predicted values of the coercive force for alloys with cobalt content exceeding 8 mass percent ($\langle h\rangle > 0{,}4$ μm) agree fairly well with the experimental values.

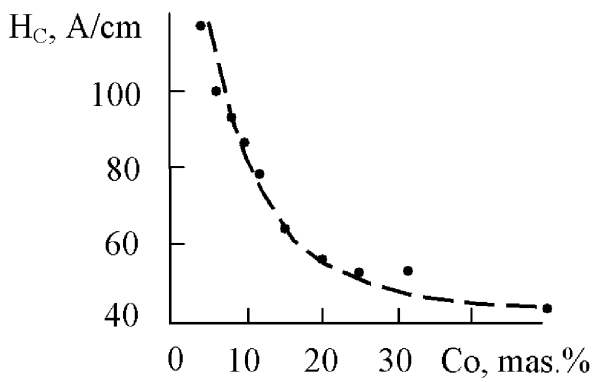


Fig. 4. H_C as dependent on cobalt content. The dashed curve shows the values of H_C predicted by eqn (9). <D> =3,25 μm

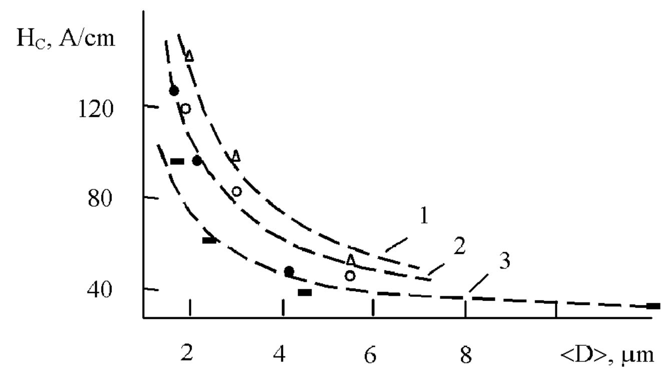
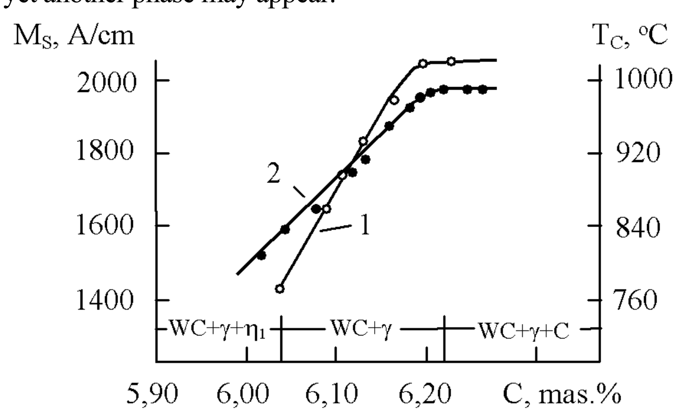


Fig. 5. H_C as dependent on the mean size of carbide grains for alloys containing: 1 to 8; 2 to 10; 3 to 15 mass percent of Co. The dashed curves show the values of H_C predicted by eqn (9).

For alloys with cobalt content under 8 mass percent ($\langle h\rangle < 0{,}4$ μm), the experimental values of H_C differ from the calculated ones, namely, they are smaller. Conceivably the cobalt interlayer might remain continuous in low-cobalt and fine-grained alloys. However, because of its small thickness ($\langle h\rangle < \delta$), the type of domain walls changes – Bloch walls turn into Néel walls, with the magnetization vectors lying in the plane of the film. According to [7], the coercive force of films with Néel walls ceases to depend on their thickness, the value of H_C approaches to the coercive force of a massive body. This imposes a restriction on the application of eqn (9), which is applicable only to medium- and high-cobalt hard alloys.

The crucial <D>-dependence of H_C within the grain size range from 1 to 5 μm allows the coercive force to be used as a parameter for nondestructive inspection of the mean size of carbide grains after sintering of hard alloys. Note that the numerical coefficients in eqn (9) are determined empirically on experimental samples of hard tungsten-cobalt alloys. For commercial hard alloys, the mean size of carbide grains can change within a wider range than in the case of experimental samples, therefore the coefficients *a* and *b* of eqn (9) may assume somewhat different values.
The strength characteristics of hard alloys depend significantly on cobalt content. It can be quantitatively determined by measuring saturation magnetization. Magnetization curves for hard alloys have a peculiarity – linear magnetization increase in fields exceeding 1000 A/cm. This feature of magnetization curves for hard alloys is explained in [8]. It follows from the model of an alloy structure shown in fig. 1 that the cobalt interlayer comprises thin ferromagnetic plates forming a continuous framework; in the general case the plane of the plates can be both parallel and perpendicular to the direction of the field applied. Under demagnetization, shape anisotropy orients the magnetization vectors along the plane of the plates. The field applied first of all causes domain wall displacement in the plates whose planes are close to the direction of magnetization. In fields of ≈1000 A/cm the domain wall displacement processes terminate for the most part. As the field increases, the further magnetization growth is due to the turn of the magnetization vectors to the direction of the field in the plates whose plane is perpendicular to the direction of the field. Consequently, the magnetic saturation of alloys will occur in fields comparable with cobalt plate shape anisotropy fields. The evaluation of the shape anisotropy field for an infinitely thin cobalt plate in the direction perpendicular to its plane gives the order of 10 kA/cm. One should take this into consideration when developing magnetizers for nondestructive test instruments to be used for items made of hard alloys.
The cobalt interlayer in hard alloys is not pure cobalt, but a solid solution of tungsten and carbon atoms in cobalt (γ-phase) resulting from partial dissolution of tungsten carbide in cobalt. Thus, 8 to 10 mass percent of tungsten carbide can dissolve in cobalt at 1340 ^{0}C. As the temperature goes down to 1000 ^{0}C, the solubility of tungsten carbide becomes 2 to 4 mass percent. The physical properties of the γ-phase differ from the properties of pure cobalt, and they depend on the amount of carbide dissolved.
Cobalt content in actual alloys is generally below 20 to 25 mass percent, the alloy structure being a mixture of two phases – tungsten carbide and the γ-phase (WC + γ). If carbon content deviates from the stoichiometric composition of the WC-phase beyond the homogeneity region of the γ-phase in sintering, yet another phase may appear.



With excess carbon, the isolation of free carbon (WC + γ + C) takes place, whereas with scarce carbon – the isolation of a η_1-phase (WC + γ + η_1) rich in tungsten and cobalt (Co_3W_3C).The isolations of the η_1-phase make the cobalt binder brittle, this being explainable, firstly, by the brittleness of the η_1-phase, and, secondly, by the fact that some cobalt from the composition of the γ-phase

Fig. 6. The effect of carbon content in the cobalt binder on the saturation magnetization (1) and the Curie temperature (2) of the WC alloy – 10 mass. percent of Co [9]

transforms to the η_1-phase.Since the strength characteristics of the alloys decrease drastically in this case, the presence of the η_1-phase in the alloy structure is impermissible. It follows from fig. 6 that the magnitude of saturation magnetization decreases significantly as carbon content decreases with respect to the stoichiometric composition of the WC-phase within the homogeneity region of the γ-phase.

The reason is that a lack of carbon causes excess atoms of free tungsten dissolved in the cobalt binder. This results in greater parameters of the cobalt lattice, poorer exchange interaction of cobalt atoms as the interatomic distances grow, and this causes lower M_S of the alloy. When carbon content is excessive with respect to the stoichiometric composition of the WC-phase, some carbon atoms dissolve in the cobalt binder without changing the lattice parameters and the magnetic properties of cobalt, the others being isolated in the form of graphite.

The variation in the exchange interaction has a natural effect on the Curie temperature T_C of the alloys, see fig.6. Curie temperature is a phase-sensitive characteristic, it is independent of the carbide phase grain size and of cobalt content, and it is governed only by the number of tungsten and carbon atoms dissolved in the cobalt binder within the two-phase region. The lack of carbon beyond the two-phase region accompanied by the formation of the η_1-phase will cause a further decrease in saturation magnetization, as part of the cobalt is bound in the non-ferromagnetic η_1 -phase.

Conclusions: Thus, by measuring such magnetic characteristics as coercive force, saturation magnetization, Curie temperature – one can perform nondestructive testing of such structural parameters as the mean size of carbide grains and carbon content in the cobalt binder, which determine the strength properties of products made of hard tungsten-cobalt alloys.

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