MAGNETIC PROPERTY OF BINDER IN WC−Co CEMENTED CARBIDES①

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ABSTRACT

The effects of solutes of wolfram and carbon on specific saturation magnetization ($4\pi\sigma$) of cobalt have been examined on the basis of the measurement of $4\pi\sigma$ for hexagonal type α-Co and cubic type β-Co. The Co-W−C solid solution simulative alloys have been fabricated according to phase composition in WC-Co cemented carbides and the effect of its component and structure on its $4\pi\sigma$ has been discussed too. It is pointed out that the Co phase structural factor must be considered as measuring the $4\pi\sigma$ of WC-Co cemented carbides.

Key words: cobalt   WC−Co cemented carbides   Co-W−C binder   specific saturation magnetization ($4\pi\sigma$)

1 INTRODUCTION

There are two isomerides in cobalt and it is usually held that cobalt is cubic type β-Co above approximate 700 K and hexagonal type α-Co at room temperature[1]. But a lot of X-ray diffraction analysis results by the author show that cobalt is usually a mixture of the two isomerides at room temperature, just the relative amount of its two isomerides is different depending on the difference of making conditions. The binder of WC-Co cemented carbides is the Co−base Co−W−C solid solution in which wolfram and carbon were dissolved. According to ref.[2], there is an atom concentration relation between wolfram and carbon in two phase Co−WC field of WC−Co alloy:

$$[W] \cdot [C] = 8 \times 10^{-4} \qquad (1)$$

Metal cobalt is a ferromagnetic material, and its magnetism is related to its structure. The ferromagnetism is the synthetic action of demagnetism field, exchange action and anisotropy etc resulted from the atoms composing the ferromagnetism[3]. Consequently, the magnetism of the binder in WC−Co cemented carbides would be related to the solubility of wolfram and carbon in binder too. Although some countries have evaluated the quality of WC−Co cemented carbides with $4\pi\sigma$, but the difference in measured $4\pi\sigma$ data is large. Hence there hasn't been consistent standard for $4\pi\sigma$ of WC−Co cemented carbides up to now. Even though the results for magnetic reasearch of WC−Co alloy have been reported[4−7], however the structural factor haven't been noticed. The effects of composition on the magnetism has yet to be further studied.

2 EXPERIMENTAL

The raw material powders were once through reduced wolfram powder (FSSS. 1.5 μm, oxygen content 0.1 wt－%), reduced cobalt powder (see Table 1) and marketed carbon black (ash content below 0.1 wt－%, moisture content below 0.2 wt－%, volatile content below 1.5 wt－%).

Cobalt, wolfram and carbon black powders were mixed uniformly according to the proportion defined by equation (1) to make binary Co－W, Co－C and ternary Co－W－C simulative solid solution mixtures respectively. The mixtures were formed into 3 mm × 5 mm × 30 mm blocks under pressure of 98.07 MPa and were treated in solution under vacuum of 13.33～26.66 Pa at a tem. of 1,050 ℃ for 3 h then furnace cooled to room temperature.

The particle size of raw material powders was measured by Fisher apparatus. The oxygen content was analysed by weightless method in hydrogen. The D／Max－Rc X－ray Diffractometer was used to determine the phase composition of Co, Co－W, Co－C and Co－W－C.

The repacked CL6－1 direct magnetic apparatus was used to measure the saturation magnetization (M_s) at room temperature. The M_s measurement of α－Co and β－Co for two batch pure Co powders having different structural composition (see Fig.1 and Table 1) have been done by means of packing them in the open-ended dia. 4 mm × 11 mm copper tube then pressing them and weighing their mass

and measuring volume carefully to account their density exactly. The $4\pi\sigma$ was accounted from M_s by the following formula:

$$4\pi\sigma = M s(T) / \rho \qquad (2)$$

where ρ is the pressing density of cobalt powders or the sintering density of Co－W, Co－C binary solid solution and ternary Co－W－C simulative alloys. The measured results for pure cobalt were checked further by KRUPP type specific saturation magnetization apparatus.
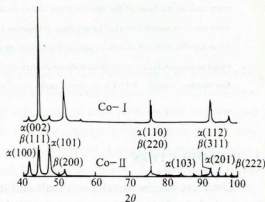

Fig. 1   X－ray diffraction patterns of Co powders

3 RESULTS AND DISCUSSION

3.1 Effect of Structural Type on Cobalt $4\pi\sigma$

The $4\pi\sigma$ was accounted from formula (2). The coupled equations for $4\pi\sigma$ were established on the basis of the structural compositions of Co－1 and Co－2 powders indicated in Table 1 to evaluate promptly the $4\pi\sigma$ of α－Co and β－Co at room temperature:

$$4\pi\sigma_{(\alpha)} = 1\ 958\ \text{A} \cdot \text{m}^2 / \text{kg}$$

Table 1   Character of Co samples

Samples	FSSS /μm	O_2/ wt－%	ρ/ g·cm^{-3}	α－Co/ wt－%	β－Co/ wt－%	Ms/ A·m^{-1}·10^{-4}	$4\pi\sigma$/ A·cm^2·kg^{-1}
Co－1	1.7	0.05	1.81	27.71	72.29	14.78	277.66
Co－2	3.2	0.05	1.81	75.21	24.79	14.39	1878

$$4\pi\sigma_{(\beta)} = 2\,070\ \mathrm{A \cdot m^2 / kg}.$$

The results show that, the $4\pi\sigma$ values of the two isomerides are distinctly different and the difference value goes beyond the error scope of CL6–1 type appatatus (Ms, $\pm 2\%$).

Cobalt is a transition-metal, its ferromagnetism is brought from the unfilled $3d$ shell and is resulted from the exchange actions of the $3d$ energy zons (the direct exchange action) and between the $3d$ and $4s$ energy zons of adjoining cobalt atoms[10]. Obviously, the $4\pi\sigma$ values of different structural cobalt are different because of the exchange actions mentioned above between atoms within cobalt unit cell are different.

3.2 *Effect of Solutes of Wolfram and Carbon on $4\pi\sigma$ of Co Binder of WC–Co*

Only the $4\pi\sigma$ value corresponding to the α-Co had been measured because of the cubic isomeride in the binary Co–W and Co–C solid solutions was negligible while making them with slow cooling rate.

The results show that the $4\pi\sigma$ value of the α-Co is increased by the solid solvation of carbon. And the relationship between the $4\pi\sigma$ of α-Co and the dissolved carbon amount corresponding to the Co binder of WC–Co is

$$4\pi\sigma_{(\alpha)} = 4\pi\sigma_{0(\alpha)} + A \cdot x_c \qquad (3)$$

where A equals to $52.50 \times 10^{-7}\ \mathrm{t \cdot m^3 / kg}$, Xc is the dissolved amount of carbon in α-Co (wt-%) (Fig. 2). $4\pi\sigma_o$ (α) is the $4\pi\sigma$ value of pure α-Co and equals to $1958 \times 10^{-7}\ \mathrm{t \cdot m^3 / kg}$ at room temperature.

The solid solvation of wolfram decreases the $4\pi\sigma$ of α-Co, the reduced magnitude is proportional to the dissolved amount of wolfram (wt-%) in α-Co;

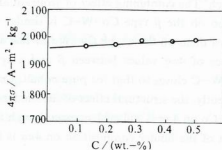$$4\pi\sigma_{(\alpha)} = 4\pi\sigma_{0(\alpha)} - B x_W \qquad (4)$$

Fig. 2 $4\pi\sigma$ of α type Co–C vs.C

where B equals to $38.89 \times 10^{-7}\ \mathrm{t \cdot m^3 / kg}$, X_w is the dissolved amount of wolfram in α-Co (wt-%). In view of $X_c \ll X_w$ in the Co phase of WC–Co cemented carbides, the result shows that wolfram far exceeds carbon in effecting the $4\pi\sigma$ of α type binder.

To obtain the $4\pi\sigma$ of ternary Co–W–C isomerides, the coupled equations for $4\pi\sigma$ must be established. Because the relative content of two isomerides in the binder of WC–Co is related to the cooling rate after sintering[8], the ternary Co–W–C alloy had been fabricated in two ways (dissolving the solid at 1,100 °C in carbon tube furnace in H_2 atmosphere for 3 h and then rapid cooling was added in addition to the method mentioned above) to make the two sets of solid solution alloy possessing different structural proportion but the same solute composition.

The results show that the effects of wolfram and carbon on the $4\pi\sigma$ of the α type Co–W–C simulative solid solution alloy is similar to the effect of wolfram on the $4\pi\sigma$ of the α type Co–W (Fig. 3). The reason is that the amount of wolfram in the simulative alloy is an inverse measure of the amount of carbon and the effect of carbon solute is insignificant. But the result shows that the composite effect of wolfram and carbon on $4\pi\sigma$ of cobalt phase are not repeated addition of individual effect

of each. The combining effect of wolfram and carbon on the β type Co—W—C is similar to that of them on the α type Co—W—C. The difference of $4\pi\sigma$ values between β and α type Co—W—C closes to that for pure cobalt. Consequently, the structural effect of the binder of WC—Co on $4\pi\sigma$ is still evident even though the effect of the binder composition on $4\pi\sigma$ is far bigger than that of its structure.
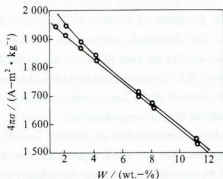

Fig. 3　$4\pi\sigma$ of α type vs.W

There are 1.7 positive holes in the unfilled $3d$ level of a cobalt atom. And the $3d$ level is low and close, more electrons can be holed in it. Cobalt atom can capture the electrons situated in the high energy s level of the solute atom possessing higher s level than it to reduce energy while the solute (e. g. wolfram) dissolves in it. The average magnetic moment μ of a cobalt atom is decided by the average amount of unfilled holes in the $3d$ level of it. Thus, when a wolfram atom replacing a cobalt atom dissolves in a cobalt cell, the extra electrons are added in the holes of $3d$ level of cobalt atom. The more the solute wolfram in cobalt, the more the reduced magnitude for average magnetic moment of cobalt atom.

On the other hand, not only the $4s$ electrons but also the interior $3d$ electrons of cobalt atom take part in bond function too[11].

There are a very few drift electrons in the $3d$ level of cobalt atom, they can drift as freely as valence electrons[9]. The drift electrons in the $3d$ level of cobalt atom could be immediately turned into "common electrons" after non-metallic carbon atoms dissolve into cobalt cell. It is signified that the unfilled holes in $3d$ level of cobalt atom increases. Thus the average magnetic moment of its atom increases. But, the solid solubility of carbon in the binder of WC—Co is small ($<$0.6wt-%), therefore the effect of carbon solute on the $4\pi\sigma$ value of Co binder is far less than that of wolfram.

4　CONCLUSIONS

(1) The $4\pi\sigma$ of cobalt and Co binder of WC—Co cemented carbides is related to their crystal structure, and the difference in $4\pi\sigma$ between the two isomerides is evident.

(2) The effect of solute wolfram on $4\pi\sigma$ of Co binder in WC—Co is opposite that of carbon. The effect of carbon on $4\pi\sigma$ of Co binder is far less than that of wolfram in two phase Co—WC.

(3) The effect of cobalt binder structure of WC—Co alloy on the $4\pi\sigma$ of it is less than that of its composition but nonnegligible.

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