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LETTER TO THE EDITOR

A NOTE ON THE EXISTENCE OF A HYPOTHETIC HIGH-TEMPERATURE H. C. P. COBALT ALLOTROPE

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Cobalt samples quenched from the melt contain CoO precipitates. This fact is a basis for a reinterpretation of the presence of presumptive high-temperature h. c. p. γ-Co allotrope in the sense of a precipitation-hardening of low-temperature ε-Co form.

A recent interpretation of the martensitic transformation of cobalt[1] stresses a decisive role of octahedrally dissolved oxygen in a dense cobalt lattice. In this letter the still unsettled question about the existence of a third, high-temperature γ-Co allotrope, stable over a temperature range above 1123—1423 K, is discussed from the same, oxygen-influence point of view.

It is well known that cobalt crystallizes in f. c. c. structure, space group $Fm3m$, with a lattice parameter $a_0 = 0.35441$ nm (α-Co)[2,3]. At 690 K, on cooling, the α-Co undergoes a martensitic transformation into the low-temperature h. c. p. phase, space group $P6_3/mmc$, with lattice parameters $a_0 = 0.2507$ nm, $c_0 = 0.4069$ nm, $c_0/a_0 = 1.623$ (ε-Co). It was Umino[4] who in early 1927 first postulated the existence of another phase, γ-Co, basing his view on the observation of a sharp decrease in the specific heat of cobalt samples at 1423 K. The generally assumed structural identity of γ-Co and ε-Co was the major obstacle of proving directly the existence of the former by quenching it from high temperatures. Studies of the crystal structure of a high-purity cobalt sample in situ, in a high-temperature

vacuum X-ray camera at temperatures up to 5 K under the melting point, made by Basinsky and Christian and communicated by Pearson[3] in 1964, appeared decisively against the existence of γ-Co, because no h. c. p. reflexion disturbed the f. c. c. diffraction pattern of α-Co. At about the same time, however, in a detailed report on quenching pure cobalt, Co-W, Co-WC and Co-C pseudoalloys[5], Kovalskii and Shalnikova claimed to have found proofs in favour of the existence of high-temperature γ-Co with a transformation temperature of 1423 K. Krainer and Robitsch[6] in 1970 continued the thirty-three years old polemics about the existence of γ-Co by their interpretation of X-ray diffraction patterns taken from a cobalt surface subjected to spark erosion. This ultra-rapid cooling technique was expected to quench properly the high-temperature γ-Co allotrope. Instead, the authors concluded that the third modification of cobalt should have a complex hexagonal unit cell belonging to the space group $P6_3mc$, with lattice parameters $a_0 = 0.8288$ nm, $c_0 = 1.0542$ nm, $c_0/a_0 = 1.272$, and with 46 atoms per cell. Krainer and Robitsch called this structure δ-Co. In the same year, however, Anantharaman[7] questioned this interpretation of diffraction patterns describing it as unusual and unconvincing. He proposed instead a much more satisfactory interpretation, by assuming the co-existence of approximately equal amounts (25% by weight) of four close-packed phases, i. e. two pure cobalt allotropes (ε-Co and α-Co) blended with two solid solutions (ε'-Co and α'-Co) of either cobalt nitride ε-Co_3N or even carbonitride γ-$Co_{24}N_7C$, in ε-Co and α-Co. Krainer and Robitsch[8] believed to have refuted this interpretation claiming that the presence of nitrogen or nitrides in their samples proved impossible. However, they mentioned the presence of faint reflexions of wustite-type cobalt oxide CoO, at least in samples prepared by spark-erosion in water. This makes one recall the old enigma of the 10.2 reflexion of ε-Co, from an early work of Edwards and Lipson[9], »which was different from other lines, and seemed to consist of a broad line with a sharper one superimposed« (Fig. 1). At the time the authors could not offer an explanation of this fact. Now it appears clear[10] that the broad line represents the actual 10.2_ε cobalt reflexion with spacing $d = 0.1480$ nm, while the sharp one should be the strong CoO reflextion 220 with a very close spacing ($d = 0.1506$ nm). Using a small, 90 nm camera with Ni$K\alpha$ radiation, the authors could not obtain these two lines clearly resolved, especially because of a considerable 10.2_ε line broadening due to the stacking faults. Reports on other experiments dealing with apparent inconsistencies on cobalt allotropy (e. g.[5,11]) also contain indications of the oxygen influence.

In the experiments[10,12] discussed in this letter, a fine, 99.9+% pure cobalt powder was vacuum sintered to dense spheres of 6—10 mm in diameter. These were levitation melted in air, in a radiofrequency (450 kHz) electromagnetic field of a conically shaped, water-cooled coil, and then dropped either in different quenching media, or between two photoelectrically activated, highly polished cemented carbide plates, fixed at the electromagnet core ends and rapidly moving towards each other. Other samples were also levitated and subsequently smashed between hardmetal plates, at a pressure of 10^2 Pa. X-ray diffraction patterns were taken by means of a standard Debye-Scherrer camera with 114.6 mm in diameter, using Co$K\alpha$ radiation with a Fe filter, or, alternatively, Mo$K\alpha$ radiation with a Zr filter. Parallely, metallographic and chromatographic analyses were carried out.

Structurally the most intriguing was the sample quenched in liquid nitrogen. When touching the liquid surface it instantaneously exploded into several black

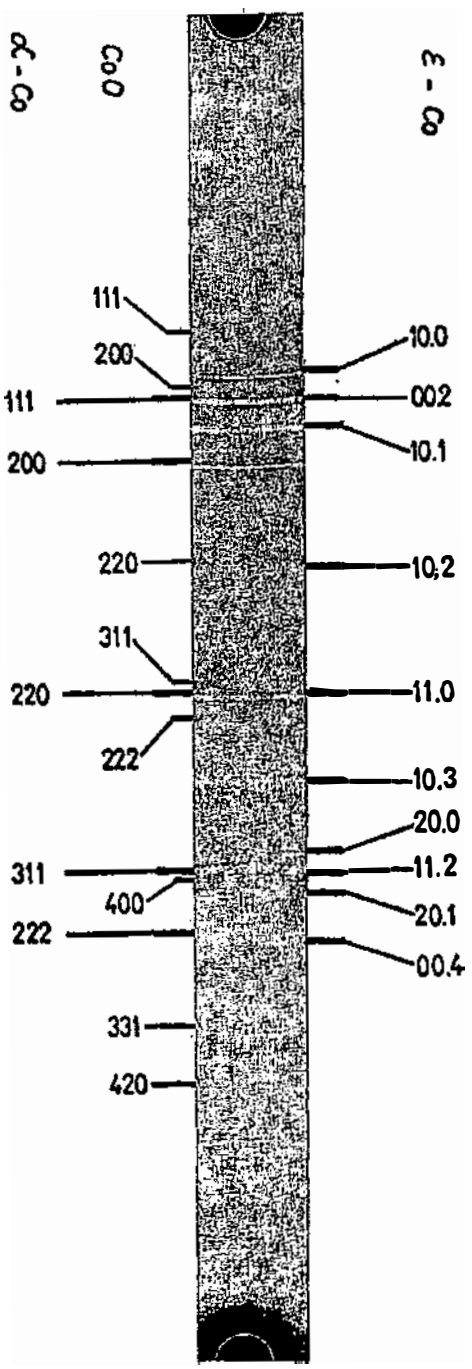

Fig. 1. Diffraction pattern of a fine cobalt powder containing both f. c. c. (α-Co) and h. c. p. (ε-Co) phase. Radiation Co$K\alpha$/Fe filter. Positions of CoO reflexions are also indicated.

fragments of a well differentiated two-phase microstructure: a very brittle, massive CoO layer up to ≈ 1 mm thick, enveloping a metallic core of the h. c. p. structure (either ε-Co or γ-Co). Isolated spherical inclusions of the metallic core phase were dispersed in the structure of CoO envelope, while a dendritic pattern of fine, rounded CoO precipitates was embedded in the structure of the core phase. In the case of the water-quenched sample the thick, compact CoO envelope was reduced to a microscopically thin film, which can be easily wiped off even by the finger. Beside well defined diffraction lines of the h. c. p. cobalt and strongest CoO lines, the X-ray diffraction photograph of this sample revealed strong lines of f. c. c. α-Co. Similar to this were X-ray diffraction photographs of the samples smashed between the hardmetal plates in air and in a rough vacuum, except for a gradual intensity increase of diffraction lines of α-Co as compared to the h. c. p. ones, and a reduction in intensity of diffraction lines of CoO. Using Sage's method[13,14] of intensity comparison of diffraction lines $200_{f.c.c.}$ and $10.1_{h.c.p.}$, one can calculate the phase composition of the samples as shown in Table 1.

TABLE 1.

Quenching medium	Vacuum	Air	Water	Liquid nitrogen
h. c. p. phase, %	59	65	89	100
f. c. c. phase, %	41	35	11	0

Phase composition of the metallic core of cobalt samples quenched in different media.

At a first glance at the Table 1 one might make a conclusion on the stabilization of high-temperature γ-Co allotrope due to the CoO precipitates. In fact, the presence of CoO precipitates might help to promote $\alpha \rightarrow \varepsilon$ martensitic transformation at equilibrium temperature (690 K); in other words, it might promote the otherwise blocked formation of the low-temperature ε-Co allotrope, which only leaves the impression of a stabilization of the presumed high-temperature γ-Co of the same crystal structure. This is supported by the dependence of the relative contents of ε-Co and α-Co phases in a fine cobalt powder on the applied external pressure, as shown in the work of Kirin et al.[15]. The percentage of ε-Co increases monotonously from about 18% in the original powder to over 80% in the green compact pressurized at 660 MPa. By extrapolation of the experimental curve given in that work one finds out that the total conversion of α-Co to ε-Co would occur at pressure of about 1200 MPa. Now, from the microstructure of the metallic core of the liquid-nitrogen quenched sample one can assess that, on average, a spherical CoO precipitate of diameter $2a \approx 1$ μm occupies the centre of a matrix cobalt spherical grain of, say, $2b \approx 6$ μm in diameter, which is comparable in size to an average particle of the powder. A solution from the elasticity theory[16], expressible through a modified formula for radial compressive stress within the cobalt grain surrounding the CoO precipitate,

$$\sigma_r = \frac{E \cdot \varepsilon_a}{(1 - 2\nu) + (1 + \nu)\frac{b^3}{a^3}} \left(1 - \frac{b^3}{r^3}\right),$$

readily applies to this ad hoc conceived structure model. Its validity is limited by the plausible assumption that there exists no outside pressure on the cobalt grain ($\sigma_{r=b} = 0$). With the elasticity modulus $E \approx 215$ GPa and Poisson's number of cobalt $\nu \approx 0.3$, one needs to know only the value of the radial compressive strain ($\varepsilon_a \equiv \varepsilon_{r=a}$) of the cobalt layers adhering to the CoO nucleus, to be able to calculate the stress. With the melting point at 2083 K, and with its relatively high solubility in molten cobalt of some 20 vol. %[17], as compared with a small solubility in solid cobalt, CoO precipitates instantaneously on solidification of cobalt melt at 1766 K. Taking for linear thermal expansion coefficients of cobalt and CoO the values 16.1×10^{-6} [18] and 12.1×10^{-6} [19] respectively, and by neglecting the low compressibility of the oxide, the boundary compressive strain of the cobalt matrix in a grain attains a value of $\varepsilon_a \approx (12.1—16.1) \times 10^{-6} \times (1766—77) \approx -68 \times \times 10^{-4}$, and the formula given above yields $\sigma_a \approx -1120$ MPa. This value is comparable to the critical applied pressure needed for the completion of the martensitic deformational transformation in the powder. Its effect is surely enhanced due to the very nature of this stress which is isotropic as it comes from the inside of the grain, in contrast to the predominantly unidirectional external compressive stress within the powder. Besides, σ_r (σ_a) is inevitably coupled with a tensile stress of half its own magnitude. Thus the residual thermal stress might be a real cause of the deformational $\alpha \rightarrow \varepsilon$ transformation in the liquid-nitrogen quenched sample. With decreasing CoO content in samples quenched in water, air or vacuum, maximum precipitation stress falls below the critical value and the transformation cannot be completed.

In conclusion, the h. c. p. phase obtained in cobalt samples quenched from high temperatures, above 1123 K, either in the experiments described here, or in most of literature, can be accepted in principle as deformation-promoted low--temperature ε-Co allotrope, formed by dispersion strengthening of the α-Co matrix around the CoO precipitates seggregated on solidification.

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O POSTOJANJU HIPOTETIČKE VISOKOTEMPERATURNE HEKSAGONSKE MODIFIKACIJE KOBALTA

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Kobaltni uzorci kaljeni iz taljevine sadrže precipitate kobaltnog oksida CoO. Ta činjenica baca novo svjetlo na hipotetičku visokotemperaturnu heksagonsku kobaltnu modifikaciju (γ-Co), koju treba shvatiti kao niskotemperaturnu fazu (ε-Co) izazvanu precipitacijskim napetostima.