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LETTER TO THE EDITOR

OXYGEN CONTROLLING COBALT ALLOTROPY

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The energetics of martensitic $\alpha \rightarrow \varepsilon$ transformation of cobalt and its reverse round an equilibrium temperature of 690 K has not yet been fully clarified. The present letter raises arguments which indicate that elastic lattice stresses, introduced by octahedral oxygen, could serve as actual regulator of cobalt allotropy.

At low temperatures up to 690 K, cobalt atoms arrange themselves in the *A*3-type (h. c. p.) structure of ε-Co with parameters $a = 0.2507$ nm, $c = 0.4069$ nm, and $c/a = 0.623$[1]. Above 690 K, thermodynamically stable is the *A*1-type (f. c. c.) α-Co with lattice parameter $a = 0.35441$ nm. A well acceptable dislocation mechanism has been proposed to describe the process of the martensitic $\alpha \rightarrow \varepsilon$ transformation on cooling, as well as its considerable temperature hysteresis in respect to the transition temperature of the reverse transformation $\varepsilon \rightarrow \alpha$ on heating[2]. Nevertheless, a striking phenomenon accompanying these transformations, i. e. the experimentally observed volume change of $(2\text{—}3.6) \cdot 10^{-3}$ in favour of the α-Co[1,3], has never been explained.

There exist quite a range of experimental data on transition temperature, for both martensite $\alpha \rightarrow \varepsilon$ transformation and its reverse, exceeding 200 K. The critical evaluation of relevant informations[4-10] indicates that either dissolved octahedral oxygen, or cobalt oxyde precipitates in a metallic matrix, influence strongly this temperature, as well as the structure of cobalt. Alternatively, from the phe-

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nomenological point of view, the structure of cobalt samples is strongly affected by mechanical stresses[11–14]. Hence, it appears plausible to assume that the temperature dependence of cobalt allotropic transformation is due to a change in elastic strains suffered by the lattice from the octahedral oxygen atoms themselves, or from the oxydes formed between them and the surrounding cobalt atoms. Certainly, this assumption implies another one, which insists on the perpetual presence of interstitial oxygen in cobalt lattice. Actually, the concept of absolutely pure metal is but a pure phantasm and metallic lattices become always, more or less, impregnated with non-metal interstitials. Depending on the value of the »interstitial ratio« ($r = r_N/r_M$) between the radii of non-metal (r_N) and metal atoms (r_M), the non-metal atom randomly occupies tetrahedral or octahedral interstices of dense metallic lattices (*A*1- and *A*3-type). Due to the inherent sphericity of metal atoms, especially cobalt ones[15], a simple lattice model based on the concept of hard atomic spheres helps to place the interstitial ratio value of a non-metal atom, which occupies an octahedral interstice of a dense metal lattice, into what is known as Hägg's interval of stable interstitial phases $0.41 \leq r \leq 0.59$[16,17]. In the case of cobalt, oxygen atom is a proper octahedral interstitial with an interstitial ratio value of $r_O/r_{Co} = 0.48$.

As to the elastic stresses introduced by octahedral interstitials, the atomic hard-sphere lattice model also provides a suitable geometrical frame for the first approach to the problem. It is an elementary octahedron of a dense metallic lattice, with six metal atoms at vertices including a non-metal in the centre, which should be considered. There are three deformational modes of interest: an isotropic expansion (labelled *f*), which from the view of crystallosymmetry is consistent with both the *A*1- and the *A*3-type lattice, and two extreme cases of exclusively *A*3--type lattice expansion, — once in dense planes {00.1} with atoms from neighbouring dense planes touching each other (labelled *h*), and then along the hexagonal axis with atoms in dense planes touching each other (labbelled *s*). The interatomic distance increase (*f*, *h*, *s*), the axial lattice ratio (*c*/*a*), and the volume (*V*) of elementary octahedron have been calculated and expressed in function of interstitial ratio (Table 1).

TABLE 1.

Expansion mode	Isotropic	In dense planes	Normal to dense planes
Interatomic distance increase	$f = r_M[\sqrt{2}(r+1)-2]$	$h = 2r_M(\sqrt{r^2+2r}-1)$	$s = 2r_M(\sqrt{r^2+2r}-1)$
Axial ratio	$\left(\frac{c}{a}\right)_f = \sqrt{\frac{8}{3}} = 1.633$	$\left(\frac{c}{a}\right)_h = \frac{2\sqrt{8r_M^2-4r_Mh-h^2}}{\sqrt{3}(2r_M+h)}$	$\left(\frac{c}{a}\right)_s = \frac{\sqrt{8r_M^2+12r_Ms+3s^2}}{\sqrt{3}\,r_M}$
Volume of elementary octahedron	$V_f = \frac{\sqrt{2}}{3}(2r_M+f)^3$	$V_h = \frac{(2r_M+h)^2}{3} \cdot \sqrt{8r_M^2-4r_Mh-h^2}$	$V_s = \frac{4r_M^2}{3} \cdot \sqrt{8r_M^2+12r_Ms+3s^2}$

Geometrical parameters for three expansion modes.

These results suggest that despite the equal interatomic distances (obviously $h = s$) in both limiting cases relating to the $A3$-type lattice, their elementary octahedron volumes differ from each other (Fig. 1). Consequently, from the standpoint of elastic energy balance, more favourable is the expansion in the basal plane $\{00.1\}$ with an axial ratio $(c/a)_h < 1.633$. Incidentally, this could be a plausible answer to the question why the majority of metals, which crystallize in an $A3$-type structure, have an axial ratio between 1.56 and 1.63[18)].

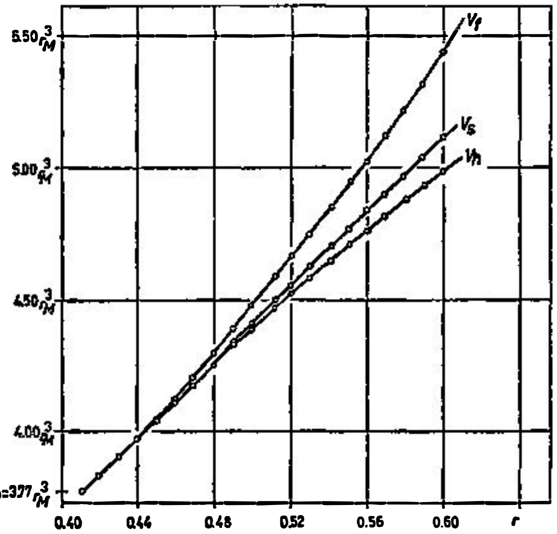

Fig. 1. Elementary octahedron volume versus interstitial ratio of Hägg's interval for three expansion modes, as calculated on the basis of Table 1.

As illustrated by Fig. 1, the elementary octahedron volume expansion is considerably higher in the isotropic mode than in the two anisotropic ones. Thus the isotropic expansion is quite unlikely to occur in the A3-type lattice, because it would introduce too great an elastic strain. In this respect much more probable are two limiting cases where $c/a \neq 1.633$. Also, simple logic suggests that deformations of the $A3$-type lattice which differ from the limitting ones, i. e. which increase all the interatomic distances although unevenly, would result in greater elementary octahedron volumes than in the limiting cases. The probability of the appearance of such expansion should, therefore, be relatively low. Summarily, the isotropic expansion of an interstitially occupied elementary octahedron has to be attributed exclusively to the $A1$-type dense lattice, while for the $A3$-type lattice only the expansion in the basal plane appears probable.

A general conclusion herefrom may be formulated as follows: an ideally pure, perfect lattice of spherical atoms should take form according to the $A1$-type crystal symmetry, in order to reflect the original sphericity of the atoms themselves. The purer the metal, the higher the probability that it will crystallize in an $A1$-type structure. The elastic strain introduced in a dense lattice by an octahedral interstitial atom is smaller in the case of the $A3$-type structure than in that of the $A1$-

-type. This means that an octahedral contaminant will stimulate crystallization in an *A*3-type structure (with $c/a < 1.633$), provided its concentration is high enough to outbalance the resistance of the crystal symmetry force field, which promotes the *A*1-type. From the standpoint of »impure metal«, the *A*3-type structure is, therefore, preferred to the *A*1-type. With rising temperature, however, the lattice expands and the octahedral non-metal obtains more space. Consequently, the interstitial ratio effectively decreases and, according to Table 1, the values of the increase of atomic distance, f and h, correspondigly diminish. The interstitial promotion of the *A*3-type structure thus suffers an adverse temperature effect which gradually erases its deformational advantages. In principle, there exists a temperature at which the overall energetic balance turns in favour of the *A*1-type lattice, which triggers off the mechanism of *A*3 → *A*1 allotropic transformation.

Let us consider cobalt sample containing 0.006 wt. % oxygen (solubility limit at low temperatures[19]): this means one oxygen atom captured within the central elementary octahedron of a cobalt cube with the edge roughly eleven *A*1-type cobalt lattice parameters long (i. e. about 5 000 cobalt atoms in all). The cube volume V_c is expressed rather through the volume $V_0 = 3.77\, r_M^3$ of the perfect (empty) elementary octahedron, $V_c = (6/4) \cdot 5\,000\, V_0 = 7\,500\, V_0$. The linear elasticity theory predicts a volume expansion of the cube (ΔV_c), as compared to the volume expansion (ΔV_0) of the oxygen-occupied central elementary octahedron, by means of ratio[20]

$$\frac{\Delta V_c}{\Delta V_0} = 3\,\frac{1 - \nu}{1 + \nu}, \tag{1}$$

which in the case of cobalt (Poisson's ratio $\nu \approx 0.3$) attains a value of 1.6. A calculation based on Table 1 shows that the *A*1-type interstitially occupied elementary octahedron, at a value of $r = 0.48$ which is characteristic of cobalt, exceeds the *A*3-type one by 1.4 vol. %, i. e. $\Delta V_0 = \Delta V_\alpha - \Delta V_\varepsilon = 1.4 \cdot 10^{-2}\, V_0$. By dividing (1) with V_0 and after inserting the given values, one readily calculates $\Delta V_c / V_c \approx$ $\approx 3 \cdot 10^{-6}$ which is negligible in comparison to the experimental value of some 10^{-3} mentioned before and thus discredits the premise.

For the work needed to expand the cube V_c by action of interstitial oxygen, the linear elasticity theory supplies the expression[20]

$$W = \frac{2}{3}\, G \left(\frac{\Delta V_0}{V_0}\right)^2 V_0, \tag{2}$$

with G designating the shear modulus ($G_{\mathrm{Co}} \approx 80$ GPa). This leads to the elastic energy difference ΔW between the isotropic *A*1-type and the basal-plane *A*3-type expansion:

$$\Delta W = \frac{2}{3}\, G \left[\left(\frac{\Delta V_0}{V_0}\right)_\alpha^2 - \left(\frac{\Delta V_0}{V_0}\right)_\varepsilon^2\right] V_0. \tag{3}$$

With $(\Delta V_0/V_0)_\alpha = 0.1461$, $(\Delta V/V_0)_\varepsilon = 0.1323$ (Table 1 for $r = 0.48$), and $V_0 =$ $= 7.4 \cdot 10^{-30}\ \mathrm{m}^3$ one obtains $\Delta W = 1.5 \cdot 10^{-21}$ J, or, dividing this by 5 000, one obtains $\overline{\Delta W}_1 \approx 3 \cdot 10^{-25}$ J/atom as the average lattice energy difference between

α-Co and ε-Co per cobalt atom, which is induced by the elastic stress due to interstitial oxygen. Again, this result is negligible in comparison to a value of $\overline{\Delta W_1} \approx$ $\approx 2 \cdot 10^{-21}$ J/atom which can be derived from the stacking fault energy of pure cobalt reaching 0.02 J/m^2 [21], and so itself discredits the premise.

It is a matter of simple logic to assume then that a change in the bonding state of interstitial oxygen, from a physical solid solute to a covalently bound oxyde nucleus, controls the allotropic transformation of cobalt. Stoichiometry that matters in a given temperature range should predominantly be Co_3O_4. Low-temperature hexagonal oxyde Co_2O_3 is unstable and cannot be prepared by dry oxydation[22], whereas the temperature stability interval of the high-temperature $A1$-type wustite-type oxyde CoO begins above 1000 K[1]. On the basis of crystallographic data the space per cobalt atom in a perfect lattice is calculated to be $11 \cdot 10^{-30}$ m^3/atom. By considering oxygen atoms as empty space and by using Table 1 (volume data at $r = 0.48$), the corresponding value of a cobalt lattice octahedrally expanded by oxygen is calculated to be $13.4 \cdot 10^{-30}$ m^3/atom. At the same time this characteristic attains a value of $22 \cdot 10^{-30}$ m^3/atom in the Co_3O_4 lattice. By repeating the algorithm of calculation $\Delta V_c/V_c$ used above, one should take into account that the covalent electronic state of the six cobalt atoms at vertices of octahedron also reflects on the 18 continuous, non-occupied elementary octahedra. Therefore all these 18 octahedra participate, at least partially, in the Co_3O_4-type expansion of the central one, increasing its deformational effect for roughly one order of magnitude. So, instead of $(22—13.4)/11 = 0.78$ one should take $\Delta V_0/V_0 \approx 10$ wherefrom, by using (1), immediately follows $\Delta V_c/V_c \approx 2 \cdot 10^{-3}$ which is in excellent agreement with the experiment. By inserting the new value $\Delta V_0/V_0$ in (3) and by dividing the result with 5 000 one readily obtains $\overline{\Delta W_t} \approx 8 \cdot 10^{-21}$ J/atom which reasonably matches the previously given experimental value of $2 \cdot 10^{-21}$ J/atom. Hence, by an abrupt change of the bonding state from ionic to covalent, the octahedral oxygen introduces enough energy in the low-temperature $A3$-type lattice, not only for the compensation of the $\varepsilon : \alpha$ lattice energy difference, but also for an abundant surplus for triggering and alimenting the transformation mechanism, whichever this may be. This time the calculation supports the premise.

It is self-understood that variations in oxygen content within the solubility limit will affect the energy balance and, consequently, cause the observed scatter in transformation temperature.

Oxydation behaviour[22], as well as conductometric properties of cobalt glass[23] and of bulk cobalt[24,25], seem to support indirectly this construct. In fact, it is not easy to imagine enough sensitive experimental method to substantiate it directly. Nevertheless, a treatment based on simple hard-shpeie lattice model can, itself, serve as an incentive for the application of more advanced methods of the solid state theory to the problem involved. The concept of covalent alteration of ionic O-Co bonding above the cobalt $\varepsilon : \alpha$ equilibrium temperature, and vice versa below that temperature, appears to be sufficiently founded in this letter and also promising enough to be further developed.

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OKTAEDRIJSKI KISIK KAO DISKRIMINANTA KOBALTNE ALOTROPIJE

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Energetika martenzitne transformacije kobalta i njezina povrata oko ravnotežne temperature od 690 K nije do kraja razjašnjena. U pismu se oživljavaju i obrazlažu argumenti u prilog hipotezi, da su elastične napetosti, unesene u rešetku oktaedrijskim kisikom, svestrani regulator ovoga fenomena.