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Crystallography of phase transitions in metastable titanium aluminium nitride nanocomposites

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ABSTRACT

The isostructural decomposition of the titanium aluminium nitride supersaturated solid solution crystallising in the face centred cubic (fcc) crystal structure into the titanium-rich fcc-(Ti,Al)N and almost titanium-free fcc-(Al,Ti)N and the transformation of metastable fcc-(Ti,Al)N into the wurtzitic aluminium nitride are discussed from the crystallographic point of view by taking the observed orientation relationships between the adjacent phases into account. It is shown that the isostructural decomposition of fcc-(Ti,Al)N into Ti-rich fcc-(Ti,Al)N and fcc-(Al,Ti)N and the transformation of the metastable fcc-(Ti,Al)N into the thermodynamically stable wurtzitic phase are concurrent processes, which are controlled not only by the thermodynamic stability of the respective compound and by the diffusivity of Al and Ti, but also by the local lattice strains. A part of the local lattice strains is regarded to result from the lattice misfit at the interfaces between the titanium aluminium nitrides having different [Al]/[Ti] concentration ratios and, in the case of the fcc/wurtzite-type interface, also having different crystal structures. The phase transition of the fcc-(Ti,Al)N to the wurtzitic one was predicted to be facilitated by stacking faults. The results of crystallographic considerations were verified experimentally by using in situ high-temperature synchrotron diffraction experiments that were performed on cathodic arc evaporated (Ti,Al)N thin films containing titanium and aluminium in different amounts.

1. Introduction

The titanium aluminium nitrides containing 50 at.% nitrogen and different fractions of Ti and Al, $Ti_{1-x}Al_xN$, belong to very frequently investigated metastable compounds. The main reason for the persistent interest in these nitrides is their technological importance, since they are employed as the main functional component of hard and high-temperature oxidation resistant protective coatings [1–4]. After the addition of aluminium to the face centred cubic titanium nitride (fcc-TiN) was shown in 1986 to improve considerably the oxidation resistance of the TiN coatings, numerous research groups made an effort to improve the oxidation resistance of (Ti,Al)N coatings further by alloying the fcc-(Ti,Al)N with other elements like vanadium [5], chromium and yttrium [6,7], silicon [8] or silicon and boron [9], ruthenium [10,11] as well as tantalum [12]. A concise overview of the influence of selected alloying elements on the properties of the quaternary and multicomponent (Ti,Al)N based coatings can be found in the review paper [13].

Almost 25 years ago, it was shown that the metastable supersaturated fcc-(Ti,Al)N undergoes spinodal decomposition into the titanium-rich fcc-(Ti,Al)N and aluminium-rich fcc-(Al,Ti)N [14], which is followed by the formation of thermodynamically stable aluminium nitride having the wurtzitic crystal structure, w-AlN. However, after the formation of w-AlN was reported to degrade both the mechanical properties of the (Ti,Al)N coatings [15–17] and their adhesion to the substrate [18], the main aim of many researchers was to avoid the thermally induced formation and growth of w-AlN in the (Ti,Al)N-based coatings. In many cases, the addition of the alloying elements listed above was intended to retard the formation of w-AlN and thus to improve the high-temperature stability and the mechanical properties of the (Ti,Al)N coatings at high temperatures. Still, there are publications showing that w-AlN should not generally be regarded as a major enemy of a high hardness. Rather, the amount and the kind of the incorporation of w-AlN in the (Ti,Al)N coatings should be considered as the main factors influencing the mechanical properties of the coatings [19–21].

In the last years, the spinodal decomposition of fcc-(Ti,Al)N into fcc-TiN and fcc-AlN was simulated by using the ab initio calculations and presented in the form of the phase diagrams describing the pseudobinary TiN-AlN system [22,23]. Moreover, some attempt was made to describe the phase stabilities in quaternary Ti–Al–X–N systems [24].

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However, the models used for the ab initio calculations are often very simplified. Therefore, they typically do not reflect the effect of the microstructure features, which are responsible for the formation and relaxation of the local strain fields, on the thermal stability of the metastable solid solutions that was described theoretically by Cahn [25] and proven experimentally for the TiN–AlN system, e.g., in references [26–29]. Still, the effect of the hydrostatic pressure on the isostructural decomposition of fcc-$Ti_{1-x}Al_xN$ was investigated in [30] that is an important step in improving the microstructure models used for the ab initio calculations.

One of the most important microstructure features that generate the local lattice strains are the internal interfaces. Already in references [14] and [31], it was shown that the coherence of neighbouring crystallites at their interfaces and the orientation relationships between the neighbouring crystallites play an important role in the phase formation during the decomposition of supersaturated (Ti, Al)N. Whereas the isostructural decomposition of supersaturated fcc-(Ti,Al)N into the Ti-rich fcc-(Ti,Al)N and fcc-AlN was observed at fully coherent interfaces, the non-coherent interfaces were found to stimulate the growth of w-AlN [31]. In the course of time, several orientation relationships between fcc-(Ti,Al)N and w-AlN were reported. In a thin film with the overall chemical composition $Ti_{0.58}Al_{0.42}N$ that was deposited using dual-target magnetron sputtering at 500 °C, Wahlström et al. [32] observed fcc-(Ti,Al)N/w-AlN interfaces having the orientation relationship $(001)_{fcc} \parallel (001)_w$ and $[1\bar{1}0]_{fcc} \parallel [\bar{1}10]_w$. The first parentheses stand for parallel lattice planes, the square brackets for parallel directions that lie within these planes.

Another orientation relationship was observed in the (Ti,Al)N coatings, which were deposited using the cathodic arc evaporation from separated Ti and Al cathodes at the substrate temperature of 450 °C [20]. In these coatings, the lattice planes $(001)_{fcc}$ and $(110)_w$ were almost parallel to each other. The mutual parallel in-plane directions were $[1\bar{1}0]_{fcc}$ and $[\bar{1}10]_w$. Finally, in (Ti,Al)N coatings deposited at the substrate temperature of 450 °C using the cathodic arc evaporation from mixed Ti–Al cathodes, the orientation relationship $(11\bar{1})_{fcc} \parallel (002)_w$ and $[1\bar{1}0]_{fcc} \parallel [100]_w$ was observed [26]. Note that for symmetry reasons, the hexagonal direction $[100]_w$ is equivalent to the crystallographic direction $[\bar{1}10]_w$, which was reported in references [20] and [32]. The above orientation relationships were usually identified by using high-resolution transmission electron microscopy (HRTEM) [26,31,32]. In some cases, the HRTEM results were seconded by the results obtained using X-ray diffraction (XRD) methods, which revealed a strong mutual orientation relationship of adjacent crystallites in dual-phase coatings that was concluded from the pronounced preferred orientation of crystallites in both phases [20,33] and from the partial coherence of the fcc crystallites [20,21,26,27,34].

In this contribution, we analyse the processes that accompany both the isostructural decomposition of the metastable supersaturated fcc-(Ti,Al)N and the formation of w-AlN at the expense of fcc-(Ti,Al)N from the crystallographic point of view. As central issues, the possible orientation relationships between fcc-(Ti,Al)N and w-AlN, the lattice strains resulting from the lattice misfit at certain habitus planes and the modification of the lattice strains via formation of microstructure defects are discussed, together with the influence of these microstructure features on the phase decomposition and on the phase transition in (Ti,Al)N. The challenges of the phase identification and the phase analysis in the dual-phase (Ti,Al)N coatings are pointed out as an important aspect of the reliability of existing experimental data.

2. Crystallographic considerations

During the spinodal decomposition of titanium aluminium nitrides into the Ti-rich and Al-rich fcc-(Ti,Al)N, both counterparts are assumed to preserve their mutual crystallographic orientation. Assuming that the lattice parameter of fcc-$Ti_{1-x}Al_xN$ depends on the aluminium contents like

$$a(Ti_{1-x}Al_xN) = [0.42418(2) - 0.01432(2) \cdot x]\ \text{nm} \tag{1}$$

(see Ref. [34]), the lattice strain, which is controlled by the lattice misfit, depends on the [Al]/[Ti] ratio in the Ti-rich and in the Al-rich fcc-(Ti,Al)N counterparts. For completely segregated fcc-TiN and fcc-AlN, the maximum lattice misfit calculated by using

$$\frac{\Delta a}{a} = 2 \cdot \frac{a_{TiN} - a_{AlN}}{a_{TiN} + a_{AlN}} \tag{2}$$

reaches approximately 3.4%. As the lattice parameter of fcc-AlN is smaller than the lattice parameter of fcc-TiN [34], the formation of fcc-AlN is accompanied by a contraction of the elementary cell of about −10%. The subsequent transformation of metastable fcc-AlN to the thermodynamically stable w-AlN with the lattice parameters $a = 0.311$ nm and $c = 0.498$ nm [35] would cause a relative expansion of the molar volume (V_M) of approximately 19% as calculated from the change in the lattice volumes recalculated to one molecule of AlN,

$$\frac{\Delta V}{V} = 2 \cdot \frac{V_M(\text{fcc}) - V_M(w)}{V_M(\text{fcc}) + V_M(w)} = 2 \cdot \frac{a_{\text{fcc}}^3/4 - \frac{\sqrt{3}}{2} a_w^2 c_w/2}{a_{\text{fcc}}^3/4 + \frac{\sqrt{3}}{2} a_w^2 c_w/2}. \tag{3}$$

However, the lattice misfit between fcc-(Ti,Al)N and w-AlN depends strongly on their mutual orientation and on the habitus planes characterising their interfaces. For the orientation relationship $(11\bar{1})_{fcc} \parallel (002)_w$ and $[1\bar{1}0]_{fcc} \parallel [100]_w$ described in [26], the distances of the corresponding lattice planes and the in-plane distances between atoms with similar in-plane symmetry are summarised in Table 1. For the sake of clarity, the distances from Table 1 are indicated in Fig. 1. From Table 1 and Fig. 1 it can be seen that the interplanar distances d_{111}(fcc) and d_{002}(w) match quite well. Still, the agreement is better for the Ti-rich fcc-(Ti,Al)N and w-AlN than for the Al-rich fcc-(Ti,Al)N and w-AlN. A similar behaviour of the lattice misfit with the Al concentration can be found also for the distances of metallic atoms within the $(11\bar{1})_{fcc}$ and $(002)_w$ planes, i.e., for the interatomic distances along the $[1\bar{1}0]_{fcc}$ and $[100]_w$ directions, and, of course, for the interatomic distances along the symmetrically equivalent directions like $[0\bar{1}\bar{1}]_{fcc}$ and $[110]_w$, $[\bar{1}0\bar{1}]_{fcc}$ and $[010]_w$, and finally $[2\bar{1}1]_{fcc}$ and $[\bar{1}10]_w$ from Fig. 1. In contrast to the distances between the neighbouring metallic atoms, the distances between the next metallic and non-metallic atoms differ seriously. Moreover, the difference in the distances between Ti/Al and N and between Al and N in fcc-(Ti,Al)N and w-AlN, respectively, is larger for Ti-rich fcc-(Ti,Al)N than for Al-rich fcc-(Ti,Al)N, see Table 1.

As supported by the crystallographic symmetry (Fig. 1) and by a relatively low lattice misfit (Table 1), the lattice planes $(11\bar{1})_{fcc} \parallel (002)_w$, $(0\bar{1}\bar{1})_{fcc} \parallel (110)_w$ and $(\bar{2}1\bar{1})_{fcc} \parallel (\bar{1}10)_w$ (as well as other symmetrically equivalent lattice planes) can be considered as possible habitus planes between the fcc and the wurtzitic structure. Still, the heteroepitaxy on the habitus planes $(11\bar{1})_{fcc}$ and $(002)_w$ leads to the highest lattice deformation, because the difference in the size of the area indicated by the black dashed lines in Fig. 1a involves the lattice misfit between $a_{fcc}/\sqrt{2}$ and a_w twice. Thus, the relative expansion of this area ranges between 7.2% and 14% in this particular case, depending on the Al content in fcc-(Ti,Al)N, cf. Table 1. For the habitus planes $(0\bar{1}\bar{1})_{fcc} \parallel (110)_w$ and $(2\bar{1}1)_{fcc} \parallel (1\bar{1}0)_w$, the relative area expansion is given by the sum of the lattice misfit in the $[1\bar{1}0]_{fcc}$ and $[100]_w$ directions, which is between 3.6% and 7%, and the lattice misfit resulting from the difference in the interplanar spacings d_{111}(fcc) and d_{002}(w), which is between 1.6% and 4.9%. Thus, for the habitus planes $(0\bar{1}\bar{1})_{fcc} \parallel (110)_w$ and $(2\bar{1}1)_{fcc} \parallel (1\bar{1}0)_w$ the relative area expansion ranges between 5.2% and nearly 12%.