

STRUCTURAL ANALYSIS OF Ti-OXYCARBONITRIDES IN V-Cr-Ti BASED ALLOYS — D.T. Hoelzer (Oak Ridge National Laboratory)

OBJECTIVE

The purpose of this work is to determine the crystal structure of globular shaped Ti-OCN (oxycarbonitrides) to assist in understanding their role in the physical metallurgy of V-Cr-Ti based alloys.

SUMMARY

A study was conducted to determine the crystal structure of Ti-OCN particles which are commonly observed in V-Cr-Ti based alloys. The information obtained from this study will be used to gain a better understanding of the physical metallurgy of the V-Cr-Ti based alloys. The precipitates examined in this study were those that formed in a V-4Cr-4Ti alloy (S-40 plate) that was annealed at 1000°C for 2 hours. The precipitates are characterized as having a globular shaped morphology with some degree of interfacial faceting. The structural analysis indicated that these precipitates are consistent with the $m\bar{3}m$ crystal point group.

INTRODUCTION

It is commonly known that an inhomogeneous distribution of Ti-oxycarbonitrides (Ti-OCN) often form in the solid solution matrix of V-Cr-Ti alloys during thermo-mechanical processing. The formation of these precipitates is significant since they have been shown to influence the ductile-to-brittle transition temperature (DBTT) of V-Cr-Ti alloy by removing interstitial elements from the matrix [1]. Furthermore, their formation may also assist in controlling grain growth during thermo-mechanical processing which can influence the mechanical properties of the V-Cr-Ti alloy. However, with the exception of chemical analysis being done on the Ti-OCN precipitates there has been very little reported regarding their crystal structure. This type of information is beneficial to understanding the precipitation process of the Ti-OCN precipitates. Thus, the purpose of this study was to apply electron diffraction techniques for determining the crystal structure of the Ti-OCN precipitates. These results will be used in a more comprehensive study of the precipitation process of the Ti-OCN.

RESULTS AND DISCUSSION

The microstructure observed in the thin foil of the V-4Cr-4Ti alloy (S-40 plate) after annealing at 1000°C for 2 hours consisted of equiaxed recrystallized grains. The matrix contained an inhomogeneous distribution of globular shaped precipitates as represented in Figure 1. The size range observed for these precipitates was typically ~ 0.1 to $0.3\mu\text{m}$. There was no apparent correlation with the formation of the precipitates on grain boundaries. The EDS analysis indicated that the globular shaped precipitates contained titanium, carbon, and oxygen [2]. The presence of nitrogen could not be ascertained due to the peak overlap of $\text{N-K}\alpha$ with $\text{Ti-L}\alpha$.

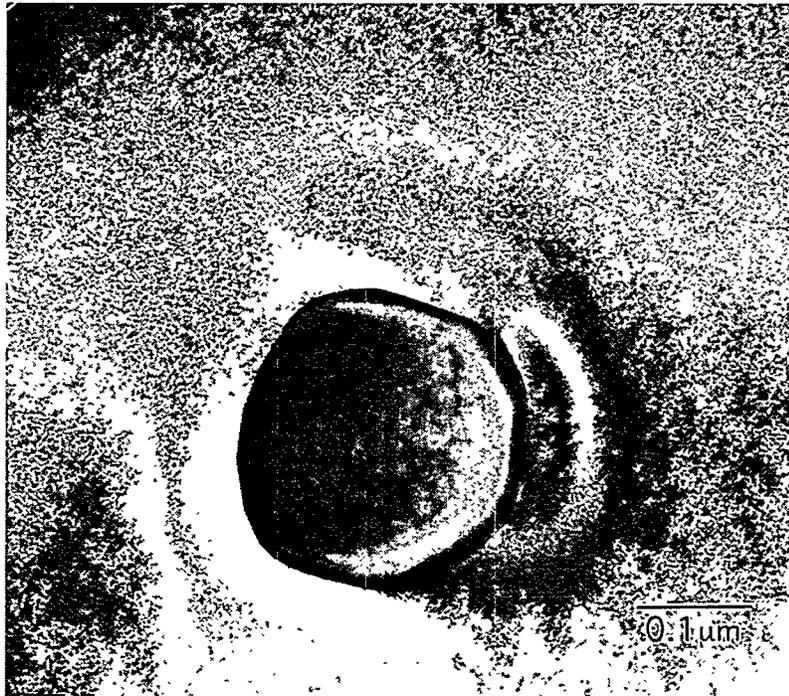
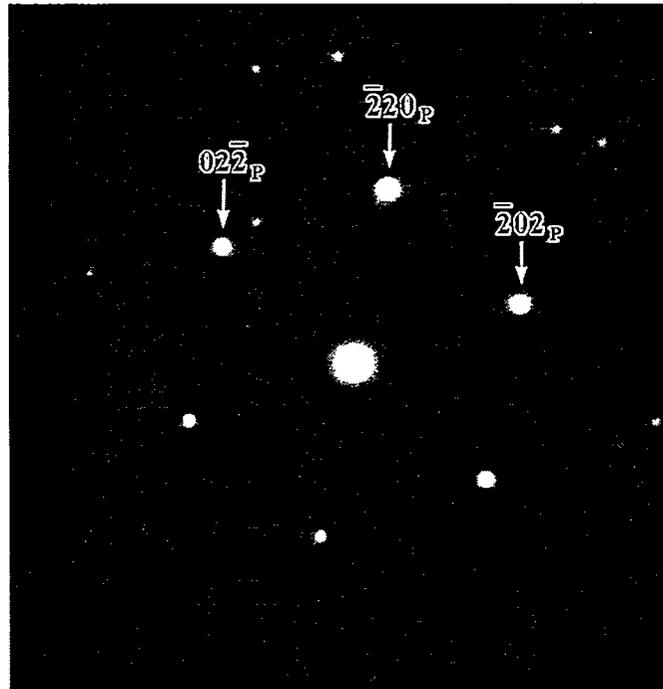


Figure 1. Globular-shaped Ti-OCN particle observed in the solid solution matrix of V-4Cr-4Ti alloys that form during thermo-mechanical processing.

The structural analysis consisted of determining the crystal point group of the precipitates. Figure 2 shows the SAED and CBED patterns that were obtained from a precipitate that was oriented along a 3-fold zone axis that could either be the $[111]$ zone axis of a cubic structure or the $[0001]$ zone axis of a trigonal/rhombohedral (hexagonal indexing) structure. The CBED whole pattern observed in Figure 2b shows HOLZ lines and Kikuchi bands that are consistent with $3m$ symmetry. The observed $3m$ symmetry rules out all possible structures except those based on either the $3m1_R$, $3m$, or $6Rmm_R$ diffraction groups [3]. There is only one crystal point group associated with the $3m1_R$ diffraction group and that is $P6m2$ which is a HCP structure. However, according to the powder diffraction files (PDF) in the international centre for diffraction data (ICDD) there are no phases present in the binary Ti-x (where $x = O, C, N$) systems that possess this point group [4]. There are two point groups associated with the $3m$ diffraction group and they are $3m$ and $\bar{4}3m$. However, there are no reported phases that exist in the binary Ti-x systems that have these point groups. The $6Rmm_R$ diffraction group is also associated with two point groups which are $\bar{3}m$ and $m3m$. From the reported phases in the binary Ti-x systems, both the α - Ti_2O_3 and β - Ti_2O_3 phases have the $R\bar{3}c$ space group which contains the $\bar{3}m$ point group. However, these two phases are eliminated as possibilities due to inconsistencies encountered when structure factor considerations are applied to the indexing of the SAED pattern shown in Figure 2a. Finally, the TiC, TiN, and γ -TiO phases are all reported to have the $Fm\bar{3}m$ space group, which contains



(a)



(b)

Figure 2. Structural analysis of the Ti-(OCN) phase showing (a) the [111] zone axis and (b) 3m CBED whole pattern symmetry that were consistent with the $m\bar{3}m$ point group of a fcc structure.

the $m\bar{3}m$ point group [5]. Therefore, the fcc crystal structure based on the $m\bar{3}m$ point and $Fm\bar{3}m$ space groups is the only one that is consistent with the results of the diffraction analysis.

A second zone axis of high symmetry was obtained from a representative precipitate and is shown in the SAED pattern of Figure 3. The analysis of this pattern indicated that both the structure factor and the measured interplanar d-spacings and angles were consistent with the $[110]$ zone axis of the fcc crystal structure based on the $Fm\bar{3}m$ space group.

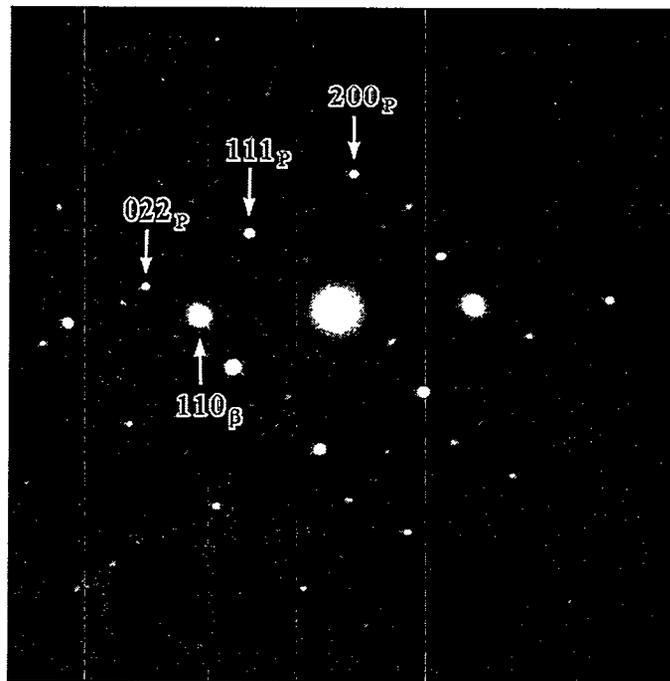


Figure 3. SAED pattern from a Ti-(OCN) particle consistent with the $[110]$ zone axis of the fcc crystal structure. The subscripts P and β denote the diffraction spots from the Ti-OCN particle and bcc solid solution matrix, respectively.

Although it is impossible to differentiate between the TiC, TiN, and γ -TiO phases based on symmetry information they may be differentiated based on lattice parameter. This is possible to an extent since the lattice parameter of each of these phases is slightly different as shown in Table 1. The lattice parameter of several precipitates was calculated from reflections present at appropriate zone axes and was found to be 4.36\AA ($\pm 0.09\text{\AA}$). From Table 1 it is seen that this value agrees the best with the lattice parameter of the TiC phase. Thus, the results of this study suggests that the Ti-OCN precipitates are based on the fcc TiC phase but that this structure can accommodate other interstitials such as O and N in solid solution. This is possible because the three binary Ti-x phases have the same $Fm\bar{3}m$ space group and are therefore isomorphous with each other.

Table 1. Compositional ranges and lattice parameters of the Ti-x (x = O, N, and C) phases.

Phase	Composition (at.%)	Space Group	Lattice Parameter	PDF Number	References
γ -TiO	34.9 to 55.5	Fm3m	4.177Å	8-0177	4,6
TiN	28 to >50	Fm3m	4.256Å	6-642	4,6
TiC	32 to 48.8	Fm3m	4.3285Å	6-614	4,6

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