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Effect of the modes of thermomechanical treatment on the formation of the multiphase and grain structure of V–4Ti–4Cr alloys

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Abstract

Transmission electron microscopy has been used to examine the microstructure of V–4Ti–4Cr alloys produced in Russia, the USA, and Japan at various stages of their thermomechanical processing. The mechanisms for phase transformations have been analyzed. The influence of phase transformations on the features of the grain structure and defect microstructure of alloys has been investigated.

1. Introduction

Vanadium alloys feature high chemical activity to interstitial impurities (C, N, O) [1]. Therefore, during the production of these alloys, they may be intensely contaminated with these impurities, and interstitial phases are formed. These phases render substantial influence on the formation of the grain structure and defect substructure of alloys, their thermal stability, propensity for low-temperature irradiation embrittlement, and other properties determining the radiation resistance of the material.

Comparative investigations of the phase-structure states formed during thermomechanical processing (TMP) of V–Ti–Cr alloys produced in Russia (V–4.36Cr–4.21Ti–0.013C–0.011N–0.02O (wt%) – alloy I), Japan (V–4.03Cr–3.73Ti–0.006C–0.008N–0.016O – alloy II), and the USA (V–3.92Cr–3.77Ti–0.017C–0.01N–0.033O – alloy III) have been performed. Electron microscopy was employed to investigate the features and mechanisms of phase transformations at different TMP stages for alloy I.

2. Experimental procedure

An ingot of alloy $I \sim 130$ mm in diameter was homogenized at $T = 1573$ K. From this ingot, by hot extrusion at $T \approx 1223$ K, a rod of about 60 mm diameter was produced which was then press forged at room temperature into a bar of thickness ~25 mm. This blank was rolled at room temperature with intermediate annealings at $T = 1273$ K and ~50% plastic strain in the intervals between annealings. Homogenizing and intermediate annealings were accomplished in a vacuum of $(1–2)\times10^5$ Torr.

Structure analysis was carried out by the methods of optical metallography and electron microscopy of thin foils and replicas with extracted second phase particles with the use of a CM30 electron microscope. The

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electron diffraction study of oxycarbonitride phases was performed accurate to ±0.001 nm.

3. Results and discussion

In alloy I in the cast state, at the boundaries and in the bulk of grains with about 1 mm in size, a high density of second phase particles having the shape of plates with thickness up to 100–150 nm and the other two dimensions up to several micrometers is observed. These plates are arranged as precipitate chains in the bulk of grains (Fig. 1) and form continuous films at the grain boundaries. Electron diffraction analysis has shown that these precipitates are particles of an fcc phase with the lattice parameter varying from 0.424 to 0.428 nm.

Comparison with the titanium and vanadium carbides, nitrides and oxides having an fcc lattice (TiC: $a \approx 0.430$ nm, V–C: 0.414 nm, TiN: 0.423 nm, VN: 0.413 nm, TiO: 0.417 nm, and VO: 0.409 nm [2]) suggests that the particles are oxycarbonitrides of variable element composition. When analyzing their structure and formation mechanism, it is necessary to bear in mind that vanadium alloys have low solubility of carbon [1] and high rate of formation of carbide phases. In VC binary systems, even at $T \approx 600$ K or during cooling after high-temperature annealings, coarse-dispersion lamellar precipitates of V_2C carbide with an hcp lattice are observed [3]. In the alloys studied in the present work, these precipitates should contain the alloying elements (Ti, Cr). With their low diffusion mobility, in comparison with carbon, and high rate of formation of the carbide phase, the concentration of the alloying elements in this phase should be close to their concentration in the alloy. Proceeding from this assumption, it can be concluded that the lamellar precipitates of the coarse-dispersion phase that are found in the ingot are titanium- and chromium-alloyed particles of vanadium oxycarbonitride with a high carbon content, and that these precipitates formed on cooling.

The microstructure of the samples of alloy I after press forging features a less uniform distribution of the oxycarbonitride phase that is less dispersed than in the ingot. The sizes of these irregularities are on the scale of some hundreds of micrometers (Fig. 2). For this case, it is possible to distinguish three types of particles of the second phases:

(1) coarse-dispersed lamellar precipitates of thickness up to 0.5–1 μm with the other two dimensions ranging from several micrometers (Fig. 3(a)) to ~10 μm;
(2) relatively equiaxial particles of a second phase (Fig. 3b) up to 1–2 μm in size, and
(3) lamellar precipitates of the oxycarbonitride phases of thickness from ~10 to 100 nm.

All these particles have an fcc lattice. The lattice parameter of the first-type precipitates is $a = 0.427$ nm. The lattice parameters of the second- and third-type particles vary over wide limits (from 0.414 to 0.436 nm), indicating that the material contains oxycarbonitride phase precipitates with a broad spectrum of compositions.

It is well known [4] that the titanium alloying to binary alloys of vanadium and interstitial elements results in a significant decrease in equilibrium solubility of nitrogen and oxygen. In this case, the stable phases are titanium-based interstitial phases. To determine the temperature intervals of solubility of these phases, we have performed a comparative study of the features of the multiphase structure of alloys I and II after thermal treatments in the temperature range $T = 1473$–1873 K, near the expected limit of solubility of the second phases. After annealings at temperatures above the limit of

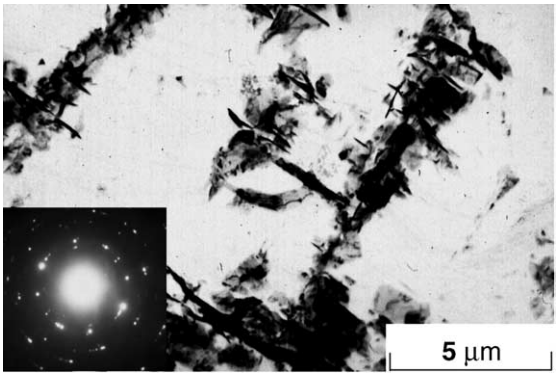

Fig. 1. Microstructure of alloy I in the cast state. Replica with extraction of the second phase.

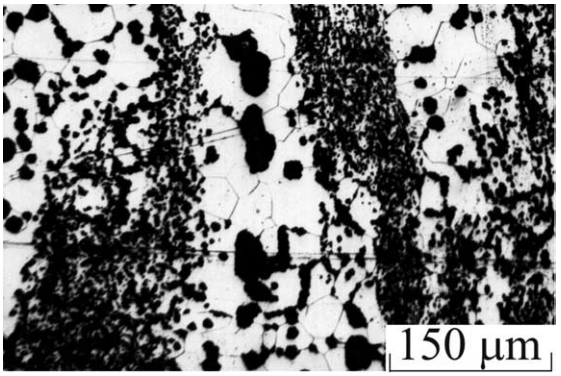

Fig. 2. Microstructure of alloy I after homogenization at $T = 1573$ K, hot extrusion, and cold press forging. Optical metallography.

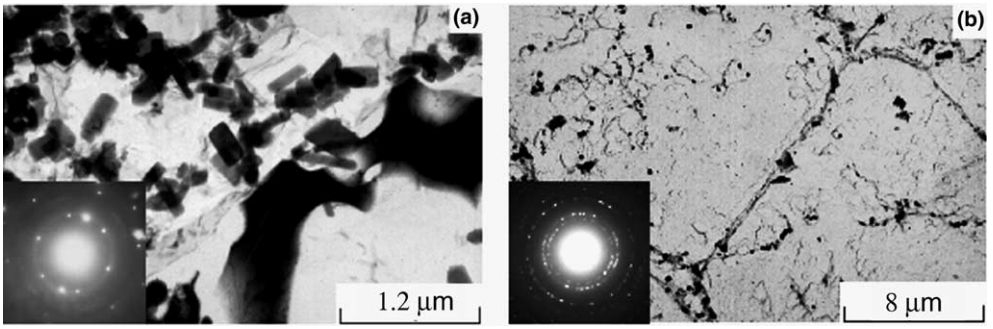

Fig. 3. Oxycarbonitride particles in alloy I after TMP in the mode presented in Fig. 2. Replicas with extraction of the second phase.

solubility, the multiphase structure is represented by metastable oxycarbonitride particles similar to those observed in the cast state. The characteristics of these particles are determined by the features of the formation of oxycarbonitrides in the course of cooling and do not depend on annealing temperature. The study has shown that in alloys I and II this type of structure is observed after thermal treatments at $T \geqslant 1773$ K. Annealing at $T = 1673$ K for an hour in the course of cooling from these temperatures results in an increase in the volume fraction of the second phase and in the formation of coarse particles similar to the first type that have been found in press forged material.

This shows that in the alloys investigated the concentration of interstitial elements exceeds their solubility limit at $T = 1673$ K, and the formation of the particles in alloy I seems to occurs during the homogenization of the ingot at $T = 1573$ K. Since titanium shows the highest chemical affinity to impurities among the elements constituting the alloy [1,5], an oxycarbonitride phase with a high titanium content should be precipitated during homogenization. The smaller equiaxial particles of the second type (Fig. 3(b)) may be the result of the formation of a similar phase during hot extrusion of an ingot. The thin lamellar precipitates of the third type seem to be particles of the metastable phase formed when the blanks were cooled after homogenization or hot extrusion. The coarse-dispersion phase formed at $T = 1573$ K prevents the homogenization of the ingot and is responsible for the high nonuniformity of the multiphase structure after press forging. The variety of mechanisms of formation of second phases results in the broad spectrum of values of the lattice parameter (from 0.414 to 0.436 nm) that is found in this state.

Since the coarse-dispersion phase with a high titanium content is thermodynamically stable, its modification during the subsequent rolling cycle is practically impossible. Therefore, the samples, until being rolled to a sheet of thickness 0.3 mm, contain both zones of uniformly distributed particles of size some tenths of a micrometer (Fig. 4(a)) and coarse plates of oxycarbonitrides (Fig. 4(b)) which are similar to those found in the structural state after press forging (Fig. 3(a)).

Electron diffraction analysis has shown that in the process of rolling the lattice parameters of oxycarbonitrides increase. In the coarse-dispersion lamellar precipitates of the second phase, these parameters increase to (0.432–0.438) nm. The finer equiaxial particles have lattice parameters of (0.428–0.430) nm. Comparison with the lattice parameters of the fcc modifications of

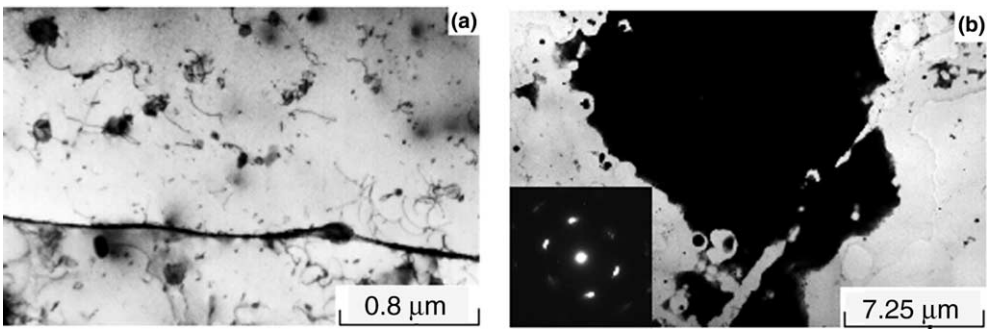

Fig. 4. Microstructure of alloy I after rolling to a sheet of thickness 0.3 mm. (a) Electron microscopy of thin foils; (b) replica with extraction of the second phase.

vanadium and titanium carbides and nitrides (see above) suggests that the reason for this increase is the increase in titanium concentration in the oxycarbonitride phase. In the finer equiaxial particles this occurs during the transformation of the metastable lamellar precipitates of the third type into a phase with a high titanium content.

In studying similar transformations in carbide-hardened niobium alloys [5] it has been shown that if the diffusion mobility of the carbide-forming elements is high enough, an in situ transformation of the type $Nb(V)C \rightarrow TiNb(V)C$ is possible. As this takes place, the active carbide-forming element (Ti) replaces niobium (vanadium) atoms in the metastable phase without dissolution of this phase. If the rate of dissolution of the metastable phase precipitates exceeds the rate of supply of titanium atoms to the reaction zone, in the vicinity of these precipitates there occurs the formation of stable carbide particles from the solid solution. If the transformation proceeds by the second mechanism, it has the features typical of processes of the internal oxidation type (carbidization) [6]. Thus, the phase transformation $VC \rightarrow TiVC$ can be considered as carbidization from internal sources (particles of metastable oxycarbonitrides), and the necessary condition for its realization is $C_C D_C / C_{Ti} D_{Ti} >> 1$ [6], where C and D are the respective concentrations and diffusion coefficients of carbon and titanium in the solid solution of the reaction zone. Examination of the value of the left side of the equation has shown that at $T = 1273$ K (temperature of the intermediate annealings in the course of TMP) this condition is not fulfilled. Hence, the most probable mechanism for the formation of stable oxycarbonitride particles is the in situ transformation of the metastable phase.

The above features of phase transformations has the result that the highly nonuniform dispersion and spatial distribution of second phases, characteristic of the structural state after press forging, persevere during the technological rolling stage. This type of nonuniformity with coarse-dispersed oxycarbonitride plates similar to those shown in Figs. 3(a) and 4(b) has been found after rolling in the alloys produced in the USA and Japan. The distinctive feature of the multiphase structure of these alloys compared to alloy I is the lower values of the lattice parameters of oxycarbonitride phases. This can be due to the variation in alloy compositions by interstitial elements and to the features of their TMP.

Electron microscopy of the grain structure and defect microstructure after TMP has shown that the particles of oxycarbonitride phases render significant influence on the processes of recovery and recrystallization. They slow down the migration of grain boundaries, pin individual dislocations (Fig. 4(a)) and small-angle boundaries, and thus control the processes of primary recrystallization and grain growth. In this case, the nonuniformity of the multiphase structure results in a substantially nonuniform grain structure of the alloys. The regions of recrystallization alternate with regions of polygonal structure (Fig. 5). Besides, rather large particles are sources of high local stresses. The traces of their plastic relaxation having the shape of sliding steps in the vicinity of grain boundaries testify that these stresses can exceed the yield point.

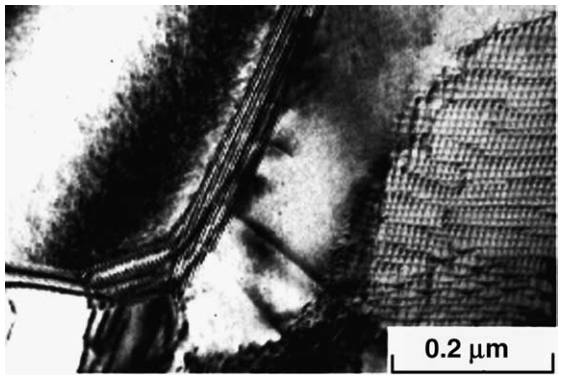

Fig. 5. Recrystallization pattern in alloy I after rolling to a sheet of thickness 0.3 mm with final annealing at 1273 K for 1 h.

4. Summary

The contamination of the V–4Ti–4Cr alloy with interstitial impurities results in a qualitative change of its phase diagram and makes the alloy multiphase with a complex sequence of phase transformations. The most important factors that control the character of the multiphase structure of this type of alloy are the low solubility of interstitial elements, the high rate of formation of coarse-dispersion precipitates of metastable vanadium carbides at different stages of TMP, and the mechanisms of their transformation to thermodynamically equilibrium particles of oxycarbonitride phases with a high titanium content. For the currently used TMP modes, the above factors are responsible for the high nonuniformity of the multiphase and grain structures. In all alloys investigated in the present work, coarse-dispersion precipitates of oxycarbonitrides of thickness up to 0.5 μm with other two dimensions of up to several tens of micrometers are observed.

Acknowledgements

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