Influence of Condensation Temperature on Microstructure and Tensile Properties of Titanium Sheet Produced by High-Rate Physical Vapor Deposition Process

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The influence of condensation temperature from 1000° to 275°C on the microstructure and tensile properties of titanium sheet produced by the high-rate physical vapor deposition process was studied. Deposition rates of 1 mil (250,000Å) per min were obtained. The microstructure varied with decreasing condensation temperature in the following sequence: above 883°C, transformed β; from 883° to 850°C, coarse columnar α; around 840°C, predominantly whisker growth; below 740°C, fine columnar α; below 450°C, very fine grained columnar α of less than theoretical density. The yield strength of the distilled sheet from 27,000 psi to 62,000 psi as the grain diameter decreased from 32 to 1 μ. The yield strength vs (grain diameter)$^{-1/2}$ plot is linear.

THE objective of this investigation was to study the influence of condensation temperature on the microstructure and mechanical properties of titanium sheet produced by high-rate physical vapor deposition. Deposition rates of 0.001 in./min (250,000Å/min) were employed. In an earlier study, Bunshah and Juntz[1] presented experimental details for the production of titanium sheet by high-rate physical vapor deposition using electron beam heating in a high-vacuum environment. They showed that full-density titanium sheet that had properties similar to cast, worked, and annealed material could be produced by this process.

EXPERIMENTAL DETAILS

The experimental setup used for this investigation is shown schematically in Fig. 1. The evaporant, a 1 in. diam commercial purity (A-70 grade vacuum arc melted) titanium rod, was contained in an electron-beam-heated rod-fed source. The titanium was vaporized and collected on a 0.018 in. thick, 3 by 3 in. stainless steel or copper substrate located 1.5 in. from the vapor source. The substrate was preheated by radiant heaters above it. The entire assembly was contained in a vacuum bell jar system maintained at a pressure between 10^{-6} and 10^{-7} torr during evaporation.

The temperature of the substrate was measured by thermocouples welded to the substrate face away from the vapor source. In a calibration experiment it was determined, by welding thermocouples to both sides of the substrate, that the temperature drop across the substrate thickness was 5°C.

The experimental procedure was as follows: Before beginning evaporation, the substrate was heated by radiant heaters to the desired condensation temperature. The condensation temperature range investigated was from 1000° to 275°C. The electron beam was then turned on and the titanium evaporated from the source and deposited on the substrate. The deposition rate in these experiments was approximately 0.001 in. (250,000Å) per min. The thickness of the deposit varied from 0.012 to 0.030 in. The substrate temperature was maintained by controlling power to the radiant heaters during evaporation.

The titanium deposit was removed from the copper substrate by dissolving the substrate in concentrated nitric acid, which does not attack titanium. Tensile and metallographic samples were taken from the center of the deposits. The tensile specimens had a gage length of 1 in. and a gage width of 0.130 in.

The condensate temperature was highest in the center, directly above the vapor source, and decreased about 100°C/in. from the center toward the edge, as indicated by thermocouples on the back of the substrate. This observation is in agreement with the cosine law, because both the vapor flux (hence, the latent heat of condensation) and the radiant heat flux from the vapor source decrease from the center toward the edge of the condensate.

RESULTS AND DISCUSSION

Chemical Analysis of the Evaporant and Distillate

Results of chemical analysis of the principal impurities in the evaporant (A-70 grade titanium rod) and the distillate are shown in Table I. Mass spectrographis techniques were used to analyze for the metallic impurities; vacuum fusion techniques for O_2, N_2, and H_2; and the combustion method for carbon. For comparison, data from the analyses of an ingot produced by vacuum electron-beam drip melting of high-purity electrolytic flake titanium produced by the U.S. Bureau of Mines and the distillate data from this high purity ingot are included in Table I.

It can be seen that considerable purification is ob-

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Table I. Chemical Analysis of Evaporant Material and Titanium Deposits Produced by Distillation (ppm by Weight)

Element	Commercial Purity A-70Ti Evaporant	Distillates From Commercial Purity A-70 Evaporant	Ingot Vacuum Melted From Electrolytic Flake	Distillates From Electrolytic Flake Vacuum-Melted Ingot
O	3000	350	200	250
C	1000	70	40	50
N	400	150	40	60
Si	400	5	15	2
Mg	1120	10	<5	<5
Fe	2000	1200	30	25
Mn	200	200	1.5	1
Co	200	10	–	–

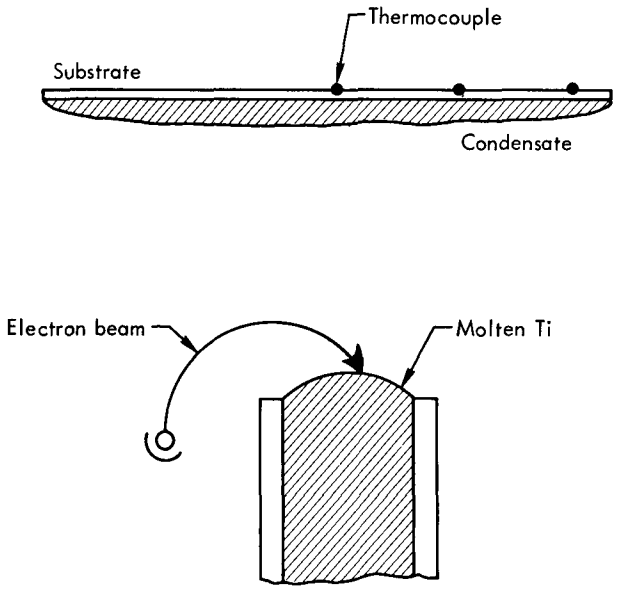

Fig. 1—Schematic of evaporation setup.

tained by distilling the commercial grade titanium. Analyses of the high-purity evaporant and distillate are about the same. The impurity content of the distillate is the sum of the purification and recontamination reactions occurring during the process. For metallic impurities, factors such as vapor pressures of the impurities and solvent, deviations from ideal solution behavior, and reevaporation of impurities from hot condensate are important. For the nonmetallic impurities, in addition to the above, contamination of the distillate from the residual gases in the vacuum environment and the formation and volatilization of metastable species (*e.g.*, TiO) from the molten pool are factors. A detailed discussion of these aspects is beyond the scope of this paper and the reader is referred to an article by Bunshah and Cocca.[2]

Influence of Condensation Temperature on Microstructure of the Deposit

The morphology of the condensate is strongly influenced by the condensation temperature. As the condensation temperature is decreased from 1000°C the microstructure undergoes changes as follows: 1) above 883°C (α-β transus temperature)—transformed β structure, 2) from 883° to 850°C—coarse columnar α, 3) around 840°C—predominant whisker growth occurs at the vapor-solid interface with subsequent thickening of the whiskers and elongated porosity; 4) below 700°C—fine columnar α with the grain size becoming finer with decreasing condensation temperature; 5) below 450°C—very fine grained columnar α of less than full theoretical density.

The changes from coarse columnar α to whisker growth to fine columnar α are not abrupt, but blend smoothly from one to the next.

The effect of various condensation temperatures on microstructure through the cross-section of the titanium deposit is shown in Fig. 2. At a condensation temperature of 900°C, which is above the transformation temperature for titanium (883°C), the structure is a "transformed β" structure. Thus, the titanium vapors condensed to β titanium, which on cooling transformed to α titanium. At condensation temperatures from 860° to 460°C, except for condensation temperatures around 840°C, the structure consists of columnar α grains. As the condensation temperature in this range decreases there is a marked decrease in grain size. In the neighborhood of 500°C, the columnar grain size becomes very fine, about 1 μ diam by 5 to 10 μ long, Fig. 3(*a*). To reveal the true columnar grain size and shape of the cross-section of the fine-grained material a special technique, sputter-etching followed by two-stage replication had to be developed.[3] In the plane of the sheet, grain shapes are polyhedral, as shown in Fig. 3(*b*). With the exception of the deposits condensed at or near 840°C, the deposits condensed at 460°C and above had full theoretical density. At condensation temperatures of 315° and 275°C the condensate had less than theoretical density with apparently interconnected longitudinal porosity. A drop of fluid on the surface of these deposits was quickly absorbed. Apparently at these low condensation temperatures and high deposition rates, surface diffusion of the incident titanium atoms is insufficient to move them to the low-energy sites to produce a fully dense deposit. Thus, growth of grains is primarily in the direction of the vapor beam leaving cavities in between.

Titanium deposits on 3 by 3 in. stainless steel substrates are shown in Fig. 4 at various condensation temperatures. The temperatures shown are at the center of each deposit. There is a temperature gradient of 100°C/in. or about 150°C in the $1\frac{1}{2}$ in. distance from the center to the edge of the deposit. Around 840°C condensation temperature, the deposit was formed by whisker growth at the vapor-solid interface, with subsequent thickening of the whiskers. The resultant columnar structure with elongated porosity is shown in Figs. 4 through 8. The predominant feature on the high-temperature deposits is a dark circular band which is a forest of whiskers. In Fig. 5 the various structures are identified on a deposit at 940°C condensation temperature. The same deposit is shown in Fig. 6 photographed at an oblique angle to show up the whisker growth. A scanning electron micrograph of the whisker forest is shown in Fig. 7. The composite photomicrograph through the cross-section, Fig. 8, shows the progression of microstructures in Fig. 5.

The reason for the change in growth morphology to predominant whisker growth around 850°C is not obvious. Normally, whisker growth is favored by low super-

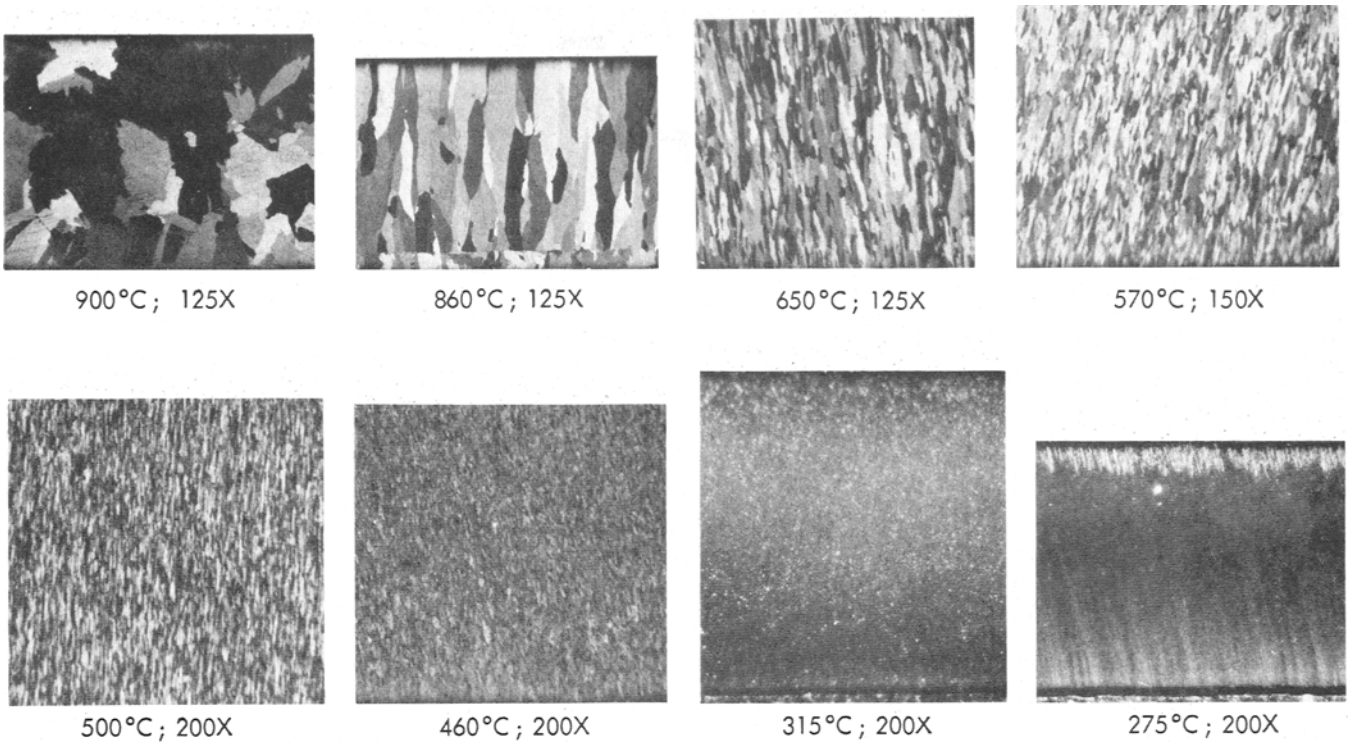

Fig. 2—Change in microstructure through cross sections of titanium deposits produced at various deposition temperatures.

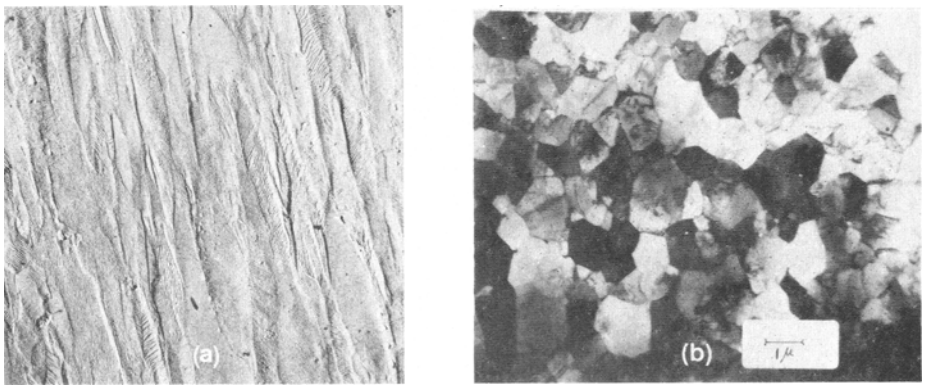

Fig. 3—Microstructure of titanium deposit produced at 500°C condensation temperature. (*a*) Cross section. Magnification 200 times. (*b*) Transmission electron micrograph in plane of the sheet.

saturation in the vapor phase. In these experiments, the vapor density was very high. It has been suggested that whisker growth may have something to do with the fact that the titanium vapor condensation temperature is close to the α-β transus temperature. This suggestion is refuted by two observations: 1) whisker growth did not occur at or near 840°C when the condensation rate was decreased from 0.001 in. (250,000Å) per min to 0.0001 in. (25,000Å) per min;[4] and 2) whisker growth also occurs at about the same condensation temperature with beryllium, whose α-β transus temperature (1220°C) is far removed from the condensation temperature. Although X-ray diffraction showed the whiskers to be single crystals, more work is needed to clarify the reason for the whisker growth mode.

Some comments on other published related work are in order. Movchan and Demchismin studied the structure and properties of thick vacuum deposits of Ti, Ni, W, Al_2O_3, and ZrO_2.[4] They found that the deposits could be divided into three characteristic structure zones with increasing condensation temperature, Fig. 9: Transition temperature T_1 between zone 1 and zone 2 is $0.3T_m$ (melting point, K) for metals; transition temperature T_2 between zone 2 and zone 3 is 0.45 to $0.5T_m$ for metals. Zone 1 has a characteristic domed structure. In cross section, the grains nucleate at various points on the substrate and increase in diameter as they grow in thickness, Fig. 9. Zone 2 consists of columnar grains with a smooth, dull surface on the deposit. Zone 3 consists of polyhedral grains and a bright surface on the deposit.

For titanium, T_1 is 390°C and T_2 is 695°C. T_1 corresponds with our observations on the transition from a fully dense columnar structure to one of less than theoretical density. On the other hand we have not observed the transition from zone 2 to zone 3 reported by Mochvan and Demchismin.[4] Moreover, it is somewhat surprising that they do not report any change in the deposit structure at the α-β transus occurring at 883°C although they varied their condensation temperatures up to 1100°C.

Marcus, Jean, and Turk[5] studied the morphology of titanium and cobalt deposited at 50,000 and 85,000Å/min from a wire-fed electron-beam source. Their deposit

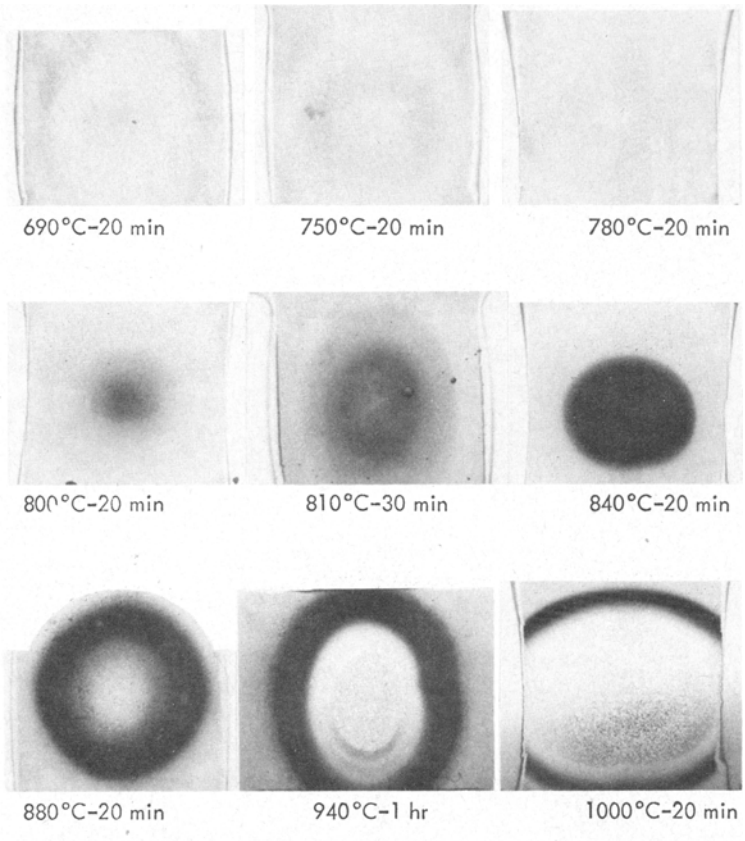

Fig. 4—Titanium deposits on 3 by 3 in. stainless steel substrates at various deposition temperatures.

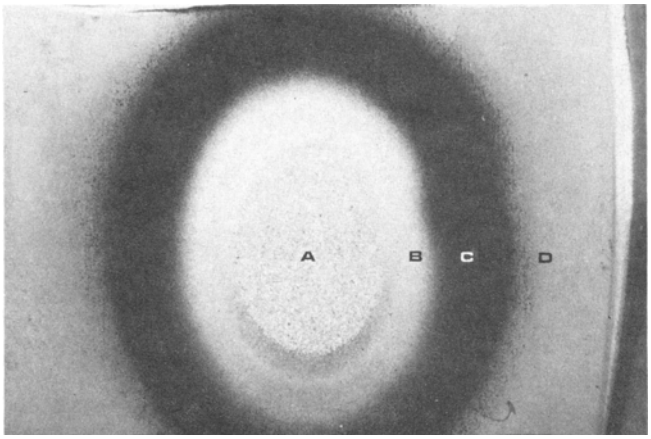

Fig. 5—Titanium deposit produced at 940°C deposition temperature: A = transformed β, B = coarse columnar α, C = whiskers, and D = fine columnar α.

had a much higher impurity content than the deposits in our investigation. Their substrate temperature was varied over a relatively narrow range of 430° to 595°C. From a study of the surface microstructure of the high deposition rate (85,000Å/min) deposit, these authors concluded that renucleation of (0001) planes occurs as evidenced by hexagonal growth patterns of 1 μ or less on the surface of the deposit. Growth then proceeds by pseudoepitaxial growth of the basal plane to form the columnar growth pattern. Their observations are in agreement with those made in this investigation, except for a minor deviation of somewhat smaller degree of renucleation in the higher purity material deposited in this investigation.

Texture and Residual Stress in the Deposits

The texture of the deposits was investigated using the Laue back reflection technique. The results showed that the deposits were lightly textured and exhibited no appreciable residual stress.

Tensile Properties vs Grain Size

The variation in tensile properties at room temperature with grain size is shown in Table II. For comparison, data from the literature on melted, worked, and annealed crystal bar titanium of comparable purity are included.[6] It is seen that for comparable grain sizes, the properties of the distilled sheet and melted rod are similar. As the grain size of the distillate decreases, both the yield strength and the tensile strength increase markedly, but the percent of elongation decreases. However, as is well recognized, percent elongation is not a true criterion of inherent ductility of the material because it depends on an arbitrary parameter, *i.e.*, the gage length. The percent reduction in area however can be a true criterion of ductility. Even at the finest grain size, its value is still 25 pct, which shows that the highest yield strength material is still quite ductile.

The yield and flow stresses of polycrystalline metals can be related to the grain size by the relationship proposed by Hall[7] and Petch,[8] *i.e.*,

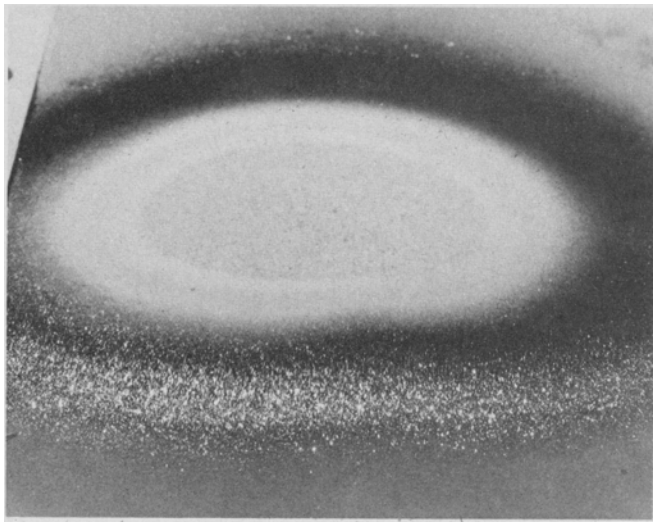

Fig. 6—Oblique view of titanium deposit shown in Fig. 5.

Fig. 7—Scanning electron micrograph of titanium whiskers. Magnification 200 times.

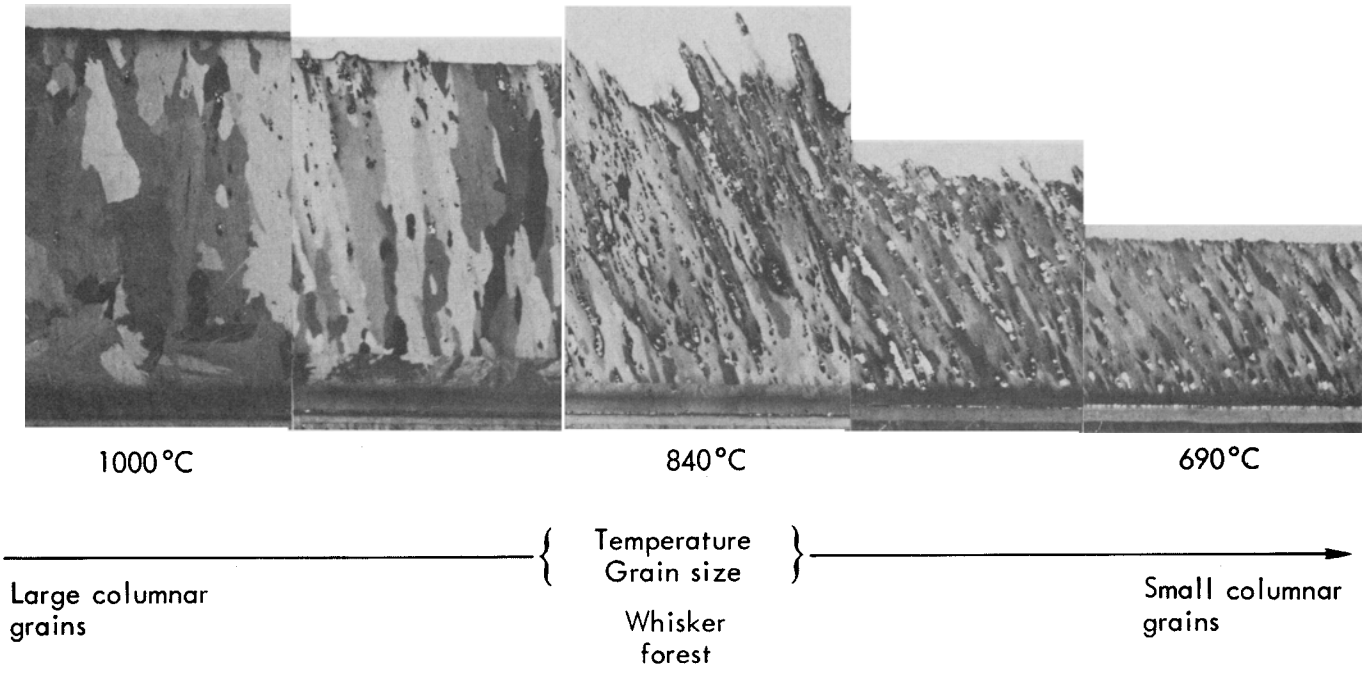

Fig. 8—Cross section of titanium deposits at various temperatures showing transition from transformed β to coarse columnar α to whisker growth and back to fine columnar α. Magnification 95 times.

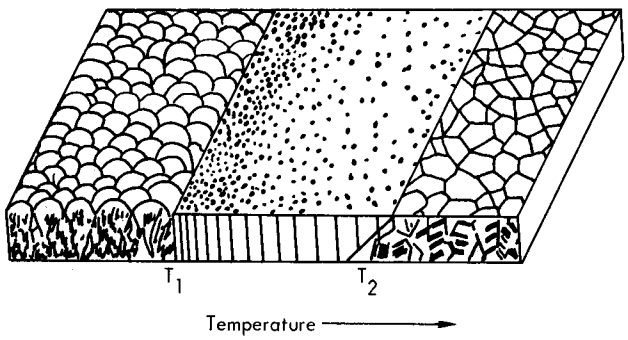

Fig. 9—Structural zones in condensate as a function of substrate temperature (after Movchan and Demchismin[4]).

$$\sigma(\epsilon) = \sigma_i + kd^{-1/2}$$

where $\sigma(\epsilon)$ is the yield or flow stress, σ_i is the friction stress, d is the grain diameter, and k the Hall-Petch slope, is a material constant.

A plot of log $\sigma(\epsilon)^{-1/2}$ is linear for many polycrystalline metals. Such a plot is shown for the yield strength of distilled titanium sheet vs grain diameter in Fig. 10 and is linear. The values of k and σ_i from the plot are 0.95 kg/mm$^{3/2}$ and 14 kg/min^2, respectively. The k value obtained is lower than the value of 1.3 kg/mm$^{3/2}$ obtained by Guard[9] and quoted by Armstrong *et al.*,[10] as compared to 48 kg/mm$^{3/2}$ obtained by Jones and Conrad.[11] In concurrence with these authors,[11] it appears that with low impurity contents in close packed

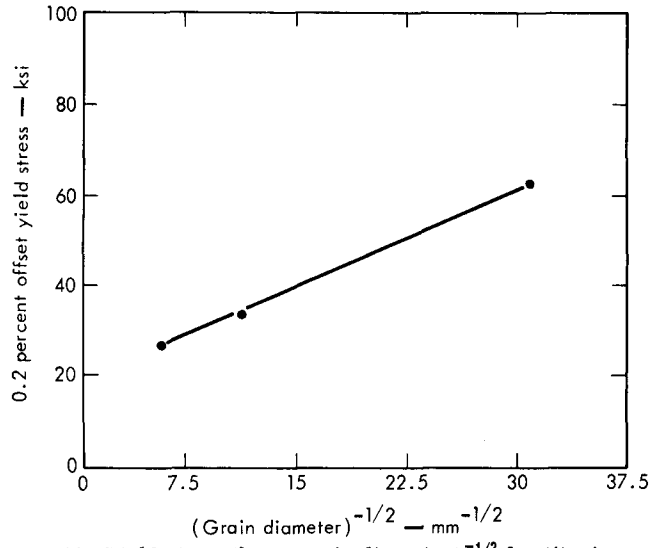

Fig. 10—Yield strength vs (grain diameter)$^{-1/2}$ for titanium deposits.

hexagonal metals, k values akin to those typical of fact centered cubic metals are obtained.

Turk and Marcus[12] obtained a yield strength of 55,000 psi in their distilled titanium sheet with 1 μ grain size, which is quite close to the value of 62,000 psi obtained in this investigation.

SUMMARY AND CONCLUSIONS

1) The influence of condensation temperature from 1000° to 275°C on the microstructure and tensile properties of titanium sheet produced by high-rate physical vapor deposition processes was studied.

2) The microstructure varied as follows: above 883°C (α-β transus temperature)—transformed β; from 883° to 850°C—coarse columnar α; around 840°C—predominant whisker growth at the vapor-solid interface with subsequent thicknening of the whiskers and elongated porosity; below 700°C—fine columnar α with grain size decreasing with condensation temperature; and below 450°C—very fine grained columnar α of less than full theoretical density.

Table II. Tensile Properties of Distilled Titanium Sheet (Average of Duplicate Samples)

Parameter	Distilled Sheet			Melted, Worked, and Annealed Crystal Bar
0.2 pct. yield strength, ksi	62	32	27	27
Ultimate tensile strength, ksi	67	43	42	43
Pct. elongation	3.0	20	25	40
Pct. reduction area	25	38	56	61
Grain size, μ				
Diameter	1	8	32	50-100
Length	10	32	140	

3) The tensile strength increases markedly with decreasing grain size increasing from 27 to 63 ksi as the grain diameter decreases from 32 to 11 μ. The ductility is good even at the finest grain size. Thus, further refining of the grain size by dilute alloying and low condensation temperature gives promise of producing a very high-strength high-toughness titanium sheet by high-rate physical vapor deposition techniques.

4) Titanium whiskers can be easily grown by high-rate physical vapor deposition techniques by maintaining the substrate at 840°C.

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