SPECIFIC HEATS OF COMMERCIAL TITANIUM ALLOYS AT 50-1100°C

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Specific-heat measurements are reported for nine titanium alloys with α and $\alpha + \beta$ structures; the temperature of the $\alpha \to \beta$ transition has been revised by DTA. A generalized approximating formula for the specific heat has been derived for the temperature range in which the structural state is stable, which contains a dimensionless parameter that includes the temperature of the $\alpha \to \beta$ transformation.

Not much is known about the specific heats of titanium alloys in relation to structure, although the temperature dependence of the specific heat provides information required in calculations on the production and use of these alloys, as well as in calculations on phase transitions and the temperature limits to the stable structures.

Three types of structure occur in titanium alloys: α, β, and two-phase $\alpha + \beta$ [1].

The temperature of the $\alpha + \beta \to \beta$ polymorphic transition is a major characteristic of a titanium alloy; it determines the temperatures used in hot working and heat treatment. Usually, the temperature is determined by trial quenching for various temperatures followed by microstructure analysis on numerous specimens.

The temperature of the $\alpha + \beta \to \beta$ transition in these alloys has been measured by DTA; we chose alloys with different types of structure that had been given the heat treatments usual for commercial titanium alloys. Table 1 gives the heat-treatment conditions and the mean chemical compositions of the alloys.

The specific heat was measured in the range 50-1100°C by a relative method with periodic heating (cooling) of the specimen and the reference material by IR filament lamps [2]. The rate of change of temperature for both specimens was measured at the instants corresponding to equality of the temperatures; the temperature dependence of the specific heat was therefore determined for discrete values, viz., by steps of 10-15°K in the region of the polymorphic transition. The reference specimen was 12Kh18N9T stainless steel, the SOTS-2 standard specimen for thermodynamic parameters [2]. The error in the specific-heat results was not more than 3% at the 0.95 confidence level.

The differential thermal analysis was performed with the specimens heated and cooled at 20°K/min at a pressure of $5 \cdot 10^{-5}$ torr. PR30/6 thermocouples with wires of diameter 0.2 mm were used. The curves were recorded with a X—Y potentiometer type PDS-021. The error in measuring the temperature of the polymorphic transition was 5°K at the 0.95 confidence level.

The DTA curves for heating and cooling are shown in Fig. 1, while Table 2 gives the $\alpha \to \beta$ transition temperatures, and Table 3 gives the smoothed values of the specific heats.

We found nearly linear temperature curves for the specific heats of α and $\alpha + \beta$ alloys at temperatures at least 100°K below the $\alpha \to \beta$ transition point; there was a more pronounced increase in the specific heat as the transition point was approached, but a fall above that point. Others have observed a rise on approaching the transition point for alloys with the same structure: for TS5 and VT3 [4] and for VT5 and VT8 [5].

An additional feature was observed for VT18 alloy, which has an elevated aluminum content: on heating over the range 500-800°C, there was an anomalous increase in the specific heat (Fig. 2). The DTA curves also indicated absorption of heat in about this temperature range (Fig. 1). The most likely cause of these effects is dissolution of the ordered α_2 phase based on Ti_3Al. This phase is formed [6,7] in titanium alloys containing more than 6% aluminum on slow cooling or on maintenance at 400-600°C; the deposition of the substance on slow cooling in this temperature range has been examined by dilatometry [8].

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TABLE 1. Heat Treatments and Mean Compositions of Titanium Alloys

Alloy	Structure type	Heat-treatment conditions	Mean chemical composition, mass %
OT4-0	Pseudo-α alloy	Anneal. at 700°C, 30 min, cooling in air	0,8 Al—0,8 Mn—Ti
VT14	α + β alloy	Anneal. at 800°C, 30 min, cooling in air	4,5 Al—5,0 Mo—1,0 V—Ti
VT16	Same	Anneal. at 780°C, 30 min, cooling with oven to 500°C, then in air	2,5 Al—5,0 Mo—5,0 V—Ti
VT22	»	Anneal. at 720°C, 30 min, cooling with oven to 350°C, then in air	5,0 Al—5,0 Mo—5,0 V—1,0 Fe—1,0 Cr—Ti
VT18	»	Anneal. at 900°C, 1 h, cooling in air	Al—Zr—Sn—Mo—Nb—Ti
VT25	»	Anneal. at 950°C, 1 h, cooling in air, anneal. at 530°C, 1 h, cooling in air	7,0 Al—2,0 Sn—1,5 Zr—2,0 V—1,0 W—Ti
VT28	»	Anneal. at 1000°C, 30 min, cooling with oven, anneal. at 600°C, 5 h, cooling in air	Al—Zr—Mo—W—Ti
VT30	Pseudo-β alloy	Tempering at 730°C for 20 min, cooling in water, aging at 550°C for 8 h, cooling in air	4,5 Sn—6,0 Zr—11,5 Mo—Ti
VT15	Same	Tempering at 800°C for 30 min, cooling in water, aging at 500°C for 15 h, heating in oven to 560°C for 15 min, cooling in air	3,0 Al—1,0 Zr—7,0 Mo—11,0 Cr—Ti

TABLE 2. Polymorphic α → β Transition Temperatures for Titanium Alloys

Alloy	$T_{\alpha\to\beta}$, °K	Alloy	$T_{\alpha\to\beta}$, °K
OT4-0	1186	BT18	1277
VT14	1230	BT25	1283
VT16	1103	BT28	1243
VT22	1093		

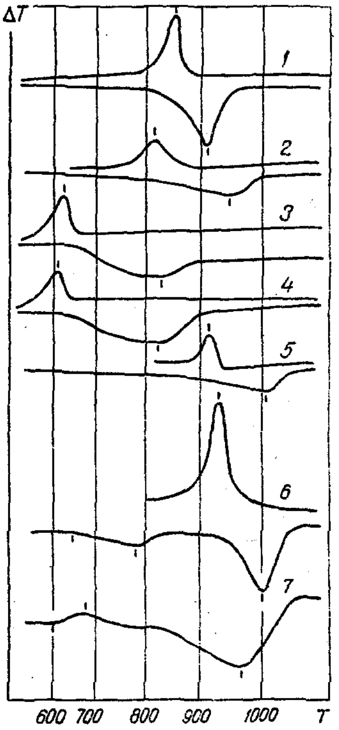

Fig. 1.

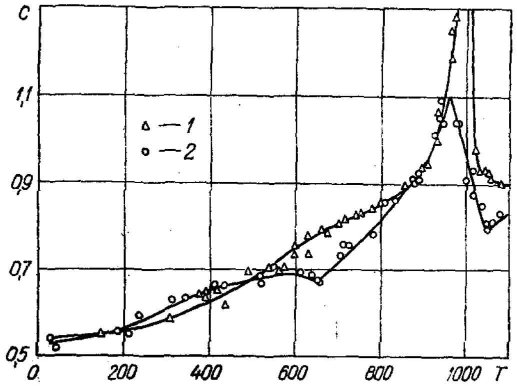

Fig. 2.

Fig. 1. DTA curves for heating and cooling of titanium alloys: 1) OT4-0; 2) VT14; 3) VT16; 4) VT22; 5) VT25; 6) VT18; 7) VT28. T is temperature (°C).

Fig. 2. Temperature dependence of the specific heat C in kJ/kg·°K for titanium alloys: 1) VT18; 2) VT28.

There is also distinctive behavior in VT28 alloy, which has an elevated tungsten content; here there is a fall in the specific heat in the range 600-700°C (Fig. 2) and the corresponding exothermic effect on the DTA curve on heating (Fig. 1). These effects appear to be related to the deposition of the δ phase at 600-700°C, which is a solid solution of titanium in tungsten [9]. The considerable rise in the specific heat above 700°C may be ascribed to dissolution of the δ phase.

The VT15 and VT30 pseudo-β alloys have no λ peak in the specific heat, and the corresponding heat effect of the polymorphic transition is absent from the DTA curves. However, the absence of these effects does not mean that there is no α + β → β transition in these alloys. Although on quenching one finds only the β phase, subsequent aging causes dispersion decomposition into α and β stable phases. X-ray analysis of VT15 before testing showed the presence of 60% of the β phase and 40% of the α phase.

The phase diagram for the Ti–Cr–Mo system implies that there is eutectoid decomposition of the β phase to give a titanium–chromium intermetallide on heating titanium alloys with high chromium contents above 600°C [10]. This corresponds to the fall in specific heat above 600°C for VT15 (Fig. 3). Therefore, for heating VT15 from 600 to 800°C one gets a eutectoid transition and a polymorphic one of α + β → α + $TiCr_2$ → β + $TiCr_2$ type. The heat

TABLE 3. Specific Heats of Titanium Alloys

Alloy	Specific heat C, kJ/kg • °K at temp. (°C) of											
	50	100	200	300	400	500	600	700	800	900	1000	1100
OT4-0	0,576	0,592	0,624	0,656	0,692	0,740	0,794	0,860	0,950 $\frac{840\ ^\circ\mathrm{C}}{1{,}100}$	2,020 $\frac{880\ ^\circ\mathrm{C}}{1{,}320}$	0,936 $\frac{880\ ^\circ\mathrm{C}}{1{,}740}$	0,960
VT14	0,620	0,640	0,678	0,716	0,756	0,796	0,835	0,884	0,950 $\frac{850\ ^\circ\mathrm{C}}{1{,}040}$	1,174 $\frac{920\ ^\circ\mathrm{C}}{1{,}624}$	1,110	1,138
VT16	0,597	0,608	0,632	0,656	0,680	0,715	0,766	0,884 $\frac{760\ ^\circ\mathrm{C}}{1{,}012}$	1,118 $\frac{780\ ^\circ\mathrm{C}}{1{,}080}$	0,990 $\frac{840\ ^\circ\mathrm{C}}{0{,}980}$	1,010	1,032
VT22	0,570	0,596	0,650	0,704	0,754	0,808	0,864	0,944 $\frac{760\ ^\circ\mathrm{C}}{1{,}045}$	1,140 $\frac{820\ ^\circ\mathrm{C}}{1{,}190}$	1,006 $\frac{840\ ^\circ\mathrm{C}}{1{,}106}$	1,032	1,078
VT18	0,544	0,548	0,560	0,582	0,622	0,674	0,742	0,804	0,850 $\frac{860\ ^\circ\mathrm{C}}{0{,}898}$	0,960 $\frac{960\ ^\circ\mathrm{C}}{1{,}142}$	1,330	0,892
VT25	0,602	0,620	0,652	0,684	0,717	0,749	0,788	0,828	0,892	1,064 $\frac{960\ ^\circ\mathrm{C}}{1{,}192}$	1,292 $\frac{980\ ^\circ\mathrm{C}}{1{,}244}$	0,990
VT28	0,536	0,540	0,565	0,603	0,642	0,674	0,694	0,716	0,814	0,958 $\frac{940\ ^\circ\mathrm{C}}{1{,}050}$	0,950 $\frac{1050\ ^\circ\mathrm{C}}{0{,}804}$	0,830
VT15	0,520	0,540	0,574	0,610	0,648	0,684	0,726	0,742	0,750	0,772	0,844	0,890
VT30	0,504	0,512	0,540	0,572	0,602	0,632	0,658	0,660	0,664	0,702	0,750	0,772

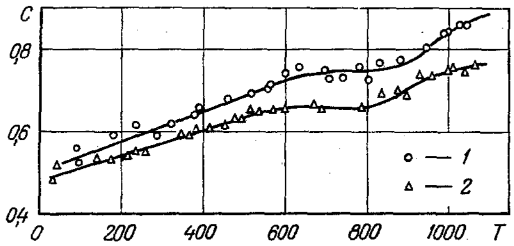

Fig. 3. Temperature dependence of the specific heat for titanium alloys: 1) VT15; 2) VT30.

of the eutectoid transition is greater than that of the α → β transition because there is only a low content of the α phase in the alloy at 600°C. Above 800°C there is a considerable increase in the specific heat, which is ascribed to dissolution of the intermetallide.

The specific heats of most of these titanium alloys OT4-0, VT14, VT16, VT18, VT25, and VT28 differ only slightly one from another in the region of the stable structural state, viz., 50-600°C; least-squares processing of the measurements for the entire group of alloys gave a single approximating equation

$$C_p = 0.450 + 0.407\,T/T_{tr} + 0.136\,(T/T_{tr})^2 \quad \text{for} \quad 350^\circ\text{K} \leqslant T \leqslant 900^\circ\text{K}$$

where C_p is the specific heat in J/g·°K and T_{tr} is the temperature of the polymorphic transition. The maximum deviation of a value calculated from this equation from the smoothed values for any of the group of alloys is 4.5%.

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