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Thermal property characterization of a Ti–4 wt.%Nb–4 wt.%Zr alloy using drop and differential scanning calorimetry

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Abstract

The thermal properties of Ti–4 wt.%Nb–4 wt.%Zr alloy, namely the enthalpy increment and heat capacity have been characterized as a function of temperature using drop and differential scanning calorimetry, respectively. The measured data clearly attested to the presence of a phase change from α (hcp) to β (bcc) phase at about 1100 ± 5 K. In fact, the alloy exhibited a transformation domain in the temperature interval 1100–1170 K. The enthalpy associated with the α → β phase change is estimated to be about 73 (±5%) J g^{-1}. The jump in the specific heat at the transformation temperature is 1714 (±7%) J kg^{-1} K^{-1}. The drop and differential scanning calorimetry results are consolidated to obtain the first experimental data on the thermodynamic quantities of this alloy.

Keywords: Metals and alloys; Enthalpy; Heat capacity; Calorimetry

1. Introduction

Titanium alloys, as a class of engineering materials have wide-ranging applications. Owing to their attractive combination of physical, chemical and mechanical properties, they find extensive use in aerospace, chemical, bio prosthetic and other high technology domains [1]. In this connection, mention must be made of a recently developed Ti–5 wt.%Ta–2 wt.%Nb alloy, which is designed as one of the probable candidate materials for the fabrication of the dissolver vessel of the fast reactor fuel reprocessing plant [2,3]. It must also be noted that materials designated for such applications should withstand the highly corrosive ambience of boiling nitric acid for a prolonged life span [2,3]. Although possessing the required corrosion resistance, the presence of tantalum in Ti–Ta–Nb alloy renders it rather expensive. In view of this fact, efforts were directed towards developing economical alternatives by replacing the costly and scarce tantalum with zirconium, yet without an undue penalty on resulting corrosion properties. Alloys belonging to Ti–Nb–Zr ternary have been considered for this purpose and one such candidate is Ti–4 wt.%Nb–4 wt.%Zr alloy [4]. The preliminary studies on this material revealed that it has nearly equal corrosion resistance as its Ti–Ta–Nb counterpart [4], recommending thereby its further development. The present study is taken up as part of a broad-based development and characterization program of Ti–Nb–Zr alloys for nuclear reprocessing applications. In specific terms, the present investigation aims at studying the basic high temperature thermodynamic characteristics, namely the temperature variation of enthalpy and specific heat capacity of Ti–4 wt.%Nb–4 wt.%Zr alloy. These quantities are measured using drop and differential scanning calorimetry techniques, respectively. The experimental details are described in Section 2.

2. Experimental details

2.1. General characterization of the alloy

The alloys were made by repeated vacuum arc melting using moderately pure titanium (99.8%), high pure (99.99%) niobium and zirconium in typically 0.6 kg batches. The composition of the final melt as determined by direct reading optical emission spectroscopy is: Ti–4 wt.%Nb–4 wt.%Zr–0.24 wt.%Fe–0.1 wt.%O. The small amount of iron originated as an impurity from titanium. This alloy,

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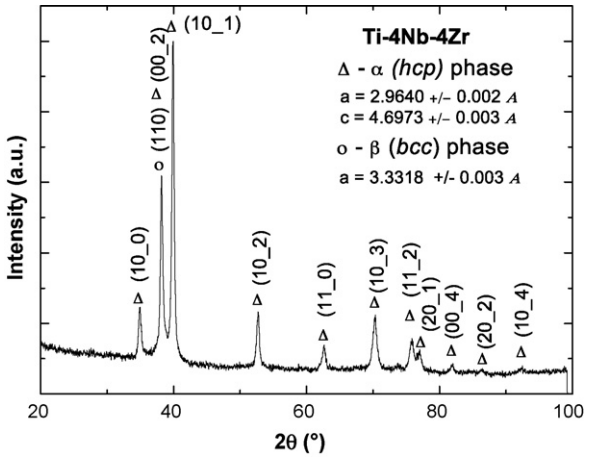

Fig. 1. Room temperature X-ray diffraction pattern of Ti–4 wt.%Nb–4 wt.%Zr alloy.

as may be judged from its nominal composition is designed to be of near α (hcp) type, although depending on the cooling rate, the presence of 4 wt.%Nb contributes small but varying amounts of β (bcc) phase to the final microstructure. The near α-nature of the alloy is certified by the room temperature X-ray diffraction pattern (Fig. 1), taken using INEL® X-ray diffraction system fitted with curved position sensitive detector having 90 degrees angular range. In addition to the predominant α phase reflections, the principal (1 0 0) reflection from the β phase is also shown in this figure. The estimated lattice parameters for the α phase are: $a = 2.964 \pm 0.002$ Å, $c = 4.6973 \pm 0.003$ Å. The lattice dimension of the cubic β phase is $a = 3.3318 \pm 0.003$ Å. The 2θ calibration is done using standard silicon sample. However, in the present study, pure titanium (Aldrich, 99.99%) has also been used and the quoted uncertainty figures for the lattice parameters correspond to that of pure titanium standard. The X-ray density of this alloy is 4.63×10^3 kg m^{-3}. The optical micrograph of the as cast structure is shown in Fig. 2. The average hardness of the alloy is found to be 230 VHN.

2.2. Drop calorimetry studies

The drop calorimetry measurements were performed using Setaram multi HTC 96® calorimeter in its drop mode. The details regarding the equipment, its calibration and data analysis procedures have been presented in our previous publications [5]. The experiment in its essence consists of instantaneously dropping a sample kept at a fixed reference temperature (T_0) to a well-equilibrated pure alumina bed maintained at the desired experimental temperature (T) to within

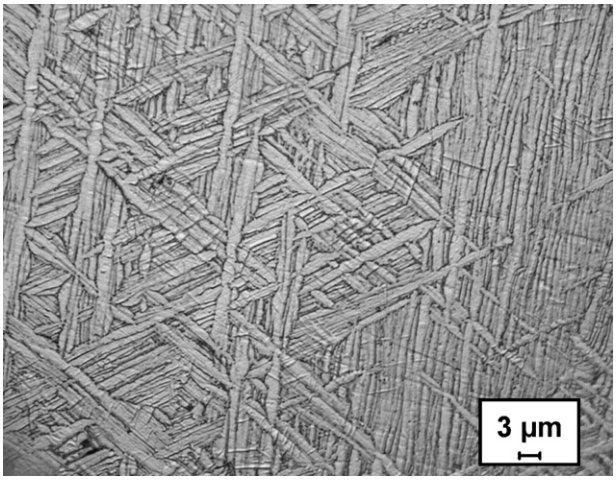

Fig. 2. Optical micrograph of the as cast structure of Ti–4 wt.%Nb–4 wt.%Zr alloy.

±1 K. Since the whole experiment is performed under quasi-adiabatic conditions and thereby presuming negligible heat loss to surroundings (other than the analysis chamber), the perturbation in the thermal equilibrium of the drop bed results in a sudden drop of its temperature, followed by a gradual rise with respect to time to its initial or preset temperature. By measuring accurately this time–temperature profile and calibrating it in terms of a similar response arising from the drop of a known mass of reference or calibration standard, it is possible to quantify the heat flux (area under the time–temperature curve) in terms of enthalpy increment [6]. A typical data collection time of about 20–30 min is maintained in the present study. An interval of about 25 min is allowed to lapse between successive drops. Considering the small mass (50–100 ± 0.1 mg) of the sample, this time is adequate enough to ensure the attainment of thermal equilibrium in the experiment. Highly pure α-Al_2O_3 was used as the calibration standard. A total of six to eight runs were performed and almost all the data points were used in the final analysis.

2.3. DSC studies

The DSC experiments were performed with Setaram Setsys 16® heat-flux type high-temperature differential scanning calorimeter, employing recrystallised alumina crucibles of about 100 μl volume. The description of the equipment and the calibration procedure has been discussed in detail in our previous publication [7]. The samples for DSC experiments were sliced from the original block using diamond coated wire saw. These were further cleaned and polished to regular and nearly identical shapes of mass varying from 40 to 120 mg. The experiments were performed under a constant flow (50 ml min^{-1}) of high pure argon. A heating rate of 10 K min^{-1} is employed. While lower than 10 K min^{-1} scans resulted in mild oxidation of the sample, higher heating rates are not normally recommended for specific heat study, especially due to the significant thermal lag between the sample temperature and that imposed by the program. While fresh samples were used for each run, multiple runs under identical conditions are performed for calibrating the precision of the measured transformation temperature. The temperature calibration is performed using recommended high pure melting point standards, namely, Sn, Al, Pb, In and Au. In addition, the measurement of enthalpy of α-hcp → β-bcc allotropic transformation in pure titanium (Aldrich, 99.99%) under identical experimental conditions is also employed for the heat flow calibration in Ti–4Nb–4Zr alloy. The heat flow rate or specific heat calibration is performed using the literature data on the specific heat of pure titanium [8–10]. The measured transformation temperatures are accurate to ±2 K; the transformation enthalpies are accurate to ±5% at 10 K min^{-1}.

A typical heat capacity measurement using DSC in the continuous heating mode involves recording of at least three consecutive, non-stop experimental runs under identical heating, holding and cooling schedule [11,12]. In the present study, a DSC run consisted of heating the system from room temperature to an initial temperature of 473 K at the rate of 10 K min^{-1} and holding at this temperature for about 15 min. This is required for the attainment of thermal equilibrium of the system before starting any measurement. This is followed by the actual programmed heating, holding and cooling cycle(s). In the present study, the sample is heated at a steady rate of 10 K min^{-1} to 1273 K, followed by an isothermal hold of about 10 min at this temperature. Subsequently, the sample is cooled to 473 K at 10 K min^{-1} and is allowed a resident time of 10 min at this temperature, before it is finally cooled again to room temperature. The three basic DSC runs that constitute a C_P measurement experiment are:

(i) the baseline run with only empty crucibles on both sides of the DSC cradle,
(ii) the reference or calibration run with the sample crucible containing high pure titanium of known mass, and
(iii) the sample run with a known mass of Ti–4Nb–4Zr alloy loaded onto the sample crucible.

It must be noted that all the three runs are performed under identical experimental conditions. In the present study, we augmented this scheme by performing one more additional baseline run at the end of the above-mentioned three run schedule. This is done in order to ensure or assess the extent of the baseline reproducibility at the end of each experimental schedule. A good agreement between the start and finish baselines is suggestive of the stable thermal dynamics of the entire DSC module and the temperature sensor. Besides it also implies