The relationship between specific heat capacity and oxidation resistance of TiAl alloys

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Properties

ABSTRACT

Purpose: The results of the measuring of the specific heat capacity of the TiAl-based alloys with the addition of Cr and Nb, in temperatures ranging from 150°C to 1000°C.

Design/methodology/approach: The measurements of the specific heat capacity have been conducted using differential scanning calorimetry method (DSC) on Setaram calorimeter. The samples, sized 15 x 9 x 1.1 mm, have been oxidized in varied thermal conditions, according to the following scheme: 2 min. of heating up to 950°C, 50 min of annealing at the given temperature, 8 min. of cooling until room temperature (25°C) was reached.

Findings: The heat resistance of the alloys under the conditions of cyclic oxidation in 950°C has been specified. Up to 800°C, the course of the cp curves agrees with Debaye model. Above 800°C, an anomaly, involving the fast increase of the cp value, can be noticed.

Research limitations/implications: Results of investigation can explain relationship between specific heat capacity and oxidation resistance of different TiAl alloy.

Originality/value: The presence of the Nb_2O_5 phase in the scale has been proved to spur the increase of the oxidation process.

Keywords: Corrosion; Oxidation resistance; Specific heat capacity; Intermetallics; TiAl

1. Introduction

Ti-Al intermetallic alloys are gaining in popularity thanks to their remarkable properties. An advantageous resistance-mass relation makes these materials notably attractive for aircraft and automotive industries. The majority of designed Ti-Al alloys are undoubtedly the most attractive light heat-resistant intermetallic compounds for aerospace applications. However, their restricted oxidation resistance at high temperatures (above 900°C), which is substantially lower than their mechanical properties, forms a serious obstacle for application of those materials [1,2]. Ti_3Al phase is invertibly ordered, while TiAl phase is stable, i.e. until melting point. TiAl possesses a relatively wide single-phase range, which isn't symmetrical as far as the chemical content is concerned. The increase of titanium concentration causes the appearance of Ti_3Al phase. Double-phase, so called „duplex"

$\gamma+(\alpha_2+ \gamma)$ alloys constitute the most common subject of material study. This is due to higher plasticity of the double-phase alloy at room temperature when compared to the single–phase one, as well as to the possibility of their production by the traditional melting, teeming, and plastic working technologies. The microstructure, which determines numerous properties of the alloy, is essential. In order to refine the grain, boron or rare earth metal modification, hot working and other types of thermal treatment are used [3].

The thermal energy provided during heating causes phase transitions in the alloys, the change in the contents' solubility, the change in the specific heat capacity, thermal conductivity and the thermal conduction coefficient. All the listed properties change to some extent as the temperature rises. In the article, the results of an investigation of specific heat capacity and heat resistance of alloys based on intermetallic phases from the Ti-Al system have been presented.

2. Experimental

The study has been conducted on double-phase Ti48Al2C2Nb, TiAl5Nb, and TiAl7Nb alloys. The chemical content of the alloys has been presented in Table 1.

Table 1.
The chemical composition of the alloys used in investigation

Alloy	The chemical composition % at.			
	Al	Nb	Cr	B
TiAlCrNb	48	2	2	
TiAl5Nb	45	5	0.2	0.2
TiAl7Nb	46	7		

The measurements of the specific heat capacity have been conducted using differential scanning calorimetry method (DSC) on Setaram calorimeter. The samples weighing 0.7g have been placed in aluminium oxide crucibles. Al_2O_3 powder has been the standard substance. The study has been conducted in argon, at temperatures ranging from 150°C to 1000°C. The heating rate was 3°C/min. The quantitative measurements have been made for the samples with a defined heat of transition, according to NIST standard. The temperature change-induced stress in the scale leads to its damage due to its cracking and dropping from the base. The degree of the scale destruction caused by the temperature change depends on the temperature difference ΔT, The temperature changing rate and the frequency of the heating-cooling cycles. The samples, sized 15 x 9 x 1.1 mm, have been oxidized in varied thermal conditions, according to the following scheme: 2 min. of heating up to 950°C, 50 min of annealing at the given temperature, 8 min. of cooling until room temperature (25°C) was reached. The samples have been weighed on the analytical balance with an accuracy to $1\cdot10^{-4}$g.

3. Results

3.1. The specific heat capacity of the alloys

As a rule, any temperature-dependent thermal phenomenon might affect specific heat capacity of the material. The specific heat capacity in invariable volume might be reduced to the following components [5]:

$$c_v = c_l + c_e + c_M + c_{other} \qquad (1)$$

where: c_l - the specific heat capacity of phonons

c_e - the specific heat capacity of conduction electrons

c_M - the specific heat capacity related to the excitation of magnetic moments (magnon)

c_{other} – the component of the specific heat capacity connected with the creation of vacancies, the order-disorder transition etc.

Figure 1 presents the specific heat capacity change curves c_p as a function of the temperature of Ti48Al2Cr2Nb, TiAl5Nb, and TiAl7Nb alloys. The c_p curves may be divided into three temperature zones: moderate (T<400°C), high (400°C<T<800°C) and ultra-high (T>800°C). The increase in the specific heat capacity at temperatures ranging from low to moderate is roughly proportional to T^3. This conduct of crystals can be well explained employing Debye model (which is also known as *the third power law)*:

$$c_v = a \cdot T^3 \qquad (2)$$

in which a is a substance-specific coefficient

TiAl5Nb alloy exhibits the specific heat capacity closest to Debye model ($c_p \sim T^{3.1}$). For Ti48Al2Cr2Nb and TiAl7Nb alloys, c_p is relatively proportional to $\sim T^{3.3}$ and $\sim T^{2.4}$. It is assumed that in the moderate range of temperatures the contribution to the specific heat capacity is mainly due to the global influence of phonons and conduction electrons located in band d, which leads to the increase of the dispersion of p-d level of titanium [5,6]. The situation is additionally complicated by the magnon contribution to c_p value. In zone III (400°C-800°C) the increase in the specific heat capacity is low or it is constant. It is supposed that in this range of temperatures the major contribution to the specific heat capacity is made by the excited phonons vibrating at a frequency equalling a constant R (R=8.31, $J\cdot mol^{-1}\cdot K^{-1}$).
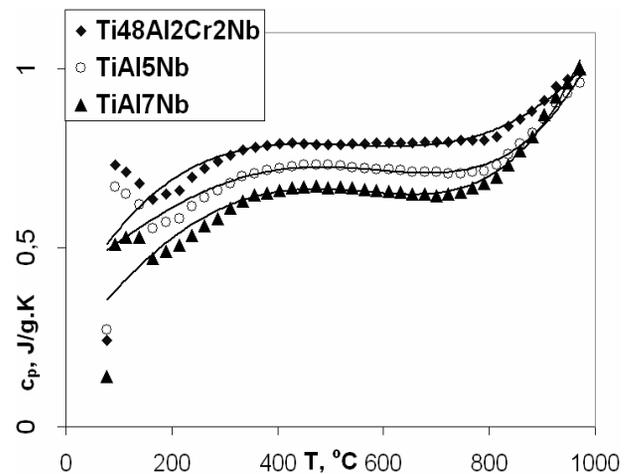
Fig. 1. The specific heat capacity of multicomponent alloys from TiAl system as a function of temperature

In ultra-high temperatures >800°C (zone III), an anomaly can be observed that involves a rapid growth of the c_p curve. A rapid growth of the specific heat capacity, characteristic of high-melting metals such as titanium, niobium or tungsten, is a result of a couple of processes. Apart from the contribution of phonons and electrons, an increased number of vacancies can affect c_p. It is

also thought that at high temperature the order-disorder transition takes place [4].

Generally, it is assumed that c_p value is higher for the phase which has lower energy bonds. This is due to the higher thermal vibration amplitude of lattice points in the given temperature [11]. High specific heat capacity value may be caused by a lower thermal gradient, which implies higher thermal shock resistance. This leads to the reduction of internal stress, which entails lower hazard of element failure.

3.2. The heat resistance of the alloys

Figure 2 shows the mass change curves after 250 oxidation cycles at the temperature of 950°C. Following the initial mass increase, decrease below the original level can be noticed in the mass of the oxidised samples.

According to Kaliszewski and Mrowec's heat resistance assessment criterion [7], the studied alloys exhibit a fairly good scale base-adherence Smialek suggests another method of assessing the durability of alloys under the conditions of cyclically varying temperature [8]. The author assumes the following parameters characterising the mass change curves:
$(\Delta m/s)_{max}$ – the maximum increase in the sample mass,
t_{max} – the time needed for reaching the maximum,
t_o – the time needed for reaching zero line,
$(\Delta m/dt)_{final}$ – a constant of final mass reduction rate.
For example, for Ti48Al2Cr2Nb alloy:
$(\Delta m/s)_{max} = 1.15 \cdot 10^{-3}$ g·cm^{-2},
$t_{max} = 82$h, $t_o = 126$h,
$(\Delta m/dt)_{final} = -0.06 \cdot 10^{-3}$ g·cm^{-2}·h^{-1} (Fig.2).

The XRD phase analysis from the surface of the samples at an angular range $2\Theta = 20-90°$ has attested that the scale in made up of TiO_2, Al_2O_3 oxides and TiN, TiAlN nitrides. In the alloy containing an additional 7 % at. of niobium Nb_2O_5 oxide is present as well (Fig. 3-5).
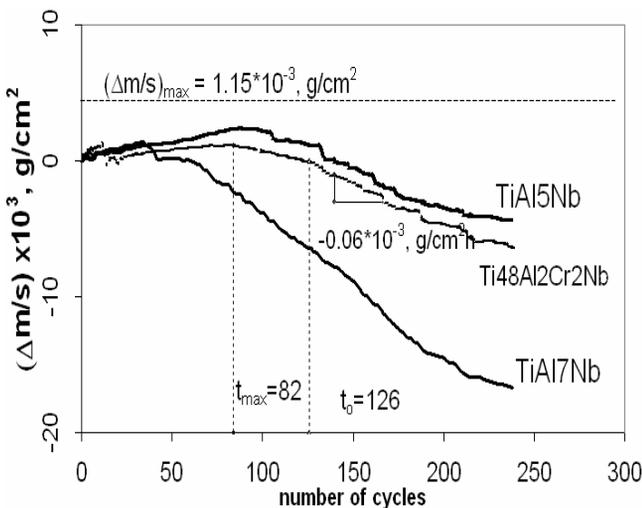
Fig. 2. The course of cyclic oxidation of multicomponent alloys from Ti-Al system. T=950°C, air (1 cycle =1h)
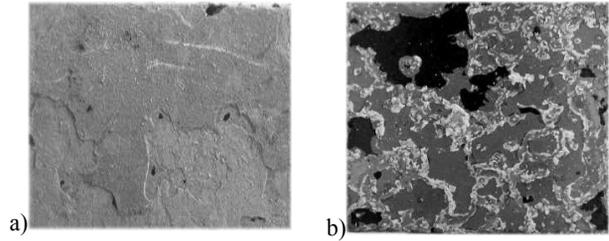
Fig. 3.The outer surface of the samples after 250 oxidation cycles. T=950°C, air. a)Ti48Al2Cr2Nb alloy, b) TiAl7Nb alloy
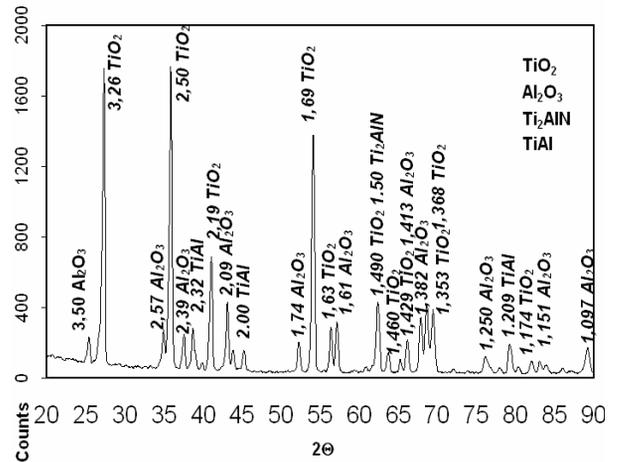
Fig. 4. A diffraction pattern of the scale formed on Ti48Al2Cr2Nb alloy after 250 oxidation cycles at 950°C
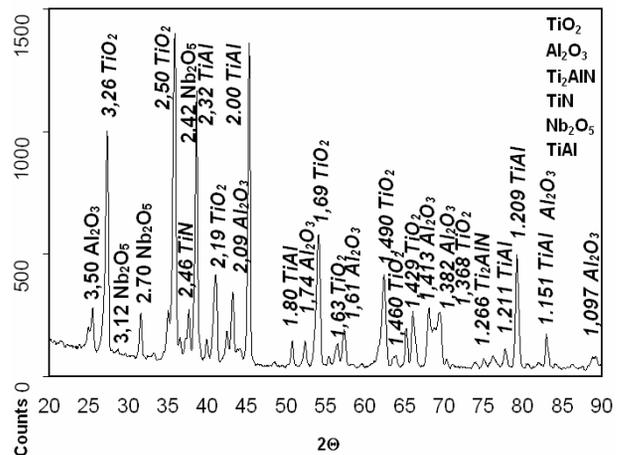
Fig. 5. A diffraction pattern of the scale formed on TiAl7Nb alloy after 250 oxidation cycles at 950°C

The mechanism of high-melting metal supplements (Nb, Hf, Ta, W) influence on the heat resistance properties of titanium alloys hasn't been explained yet, and the existing theories aren't always coherent. Rutile (natural oxide forming on titanium and its

alloys) is defective in its anion sub-lattice n. Although kations valenced more than 4 reduce the oxidation rate, their effect is insignificant, since such elements as tungsten has lower chemical affinity for oxygen than titanium. In [9] it has been observed that including $Ti_{1+x}O_{2-y}$ in the lattice of metal of oxidation state above 4^+ caused the reduction in the concentration of kation and anion sub-lattice defects. This can only be noticed when the scale is well base-adherent, and the mass transfer doesn't take place in the point defects of the kation and anion lattice. Compact, base-adherent scale may be obtained if the oxidation happens at constant temperature. During cyclic oxidation the scale cracks and peels off. If the scale formation is due to the outwards metal diffusion, the cracks may be filled up with the product of reaction. In case of the inward diffusion of the oxidiser such scale-healing processes don't take place. In this case, the diffusion of oxidiser occurs in the form of molecules and the defect structure has no significant effect on the oxidation rate. At high temperature, niobium forms a number of thermodynamically stable oxides, mainly NbO, NbO_2, Nb_2O_5. The presence of Nb_2O_5 phase is conductive to the porous scale formation [10], which might provide an explanation for the higher oxidation rate of TiAl7Nb alloy. On the other hand, as has already been stated, TiAl7Nb alloy has the lower specific heat capacity value. According to the authors of [11-15], the impact of niobium on the heat resistance increase manifests itself in the following processes:

Nb ions, replacing Ti in TiO_2, decrease the vacancy concentration in the anion sub-lattice, hindering oxygen diffusion in this way [11],

a) Nb increases the activity of Al towards Ti, which induces the formation of stable Al_2O_3 scale [12,13],

b) decreases the solubility of oxygen in the alloy, thus preventing internal oxidation [14],

c) catalises the creation of TiN, which hamper the diffusion of oxygen and titanium ions [15].

The oxidation of TiAl aluminides can be improved by protective coatings [15,16].

4. Conclusions

1. The course of the specific heat capacity curves of γ-TiAl intermetallic phase-based alloys up to 800°C roughly agrees with Debye model. Above 800°C a rapid increase in the cp value can be noticed, typical for high-melting metals such as Niobium. The contribution to the specific heat capacity comes mainly from phonons, conduction electrons and magnons.
2. In the conditions of cyclic oxidation at 950°C, the alloys exhibit a relatively good base-adherence of the scale. The presence of Nb_2O_5 oxide phase notably lowers the oxidation resistance.
3. There is a relation between the specific heat capacity and the heat resistance. The alloys possessing high specific heat capacity (Ti48Al2Cr2Nb and TiAl5Nb) have greater thermal shock resistance.

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