

High-Temperature Air Oxidation of Co-Ta Alloys – Kinetics Comparison Between TGA Information and Direct Measurement of Total Scale Thickness

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Abstract

The air oxidation of three Co-Ta alloys containing 15, 30 and 45 wt.%Ta was investigated with a thermobalance at 600, 650, 700, 750 and 800°C. In all tests the oxidation kinetics followed the parabolic rate law with the exception of Co-45Ta alloy oxidized at 800°C. The activations energies were found to be close for Co-15Ta and Co-30Ta alloys (136,11 and 128,83 kJ/mol, respectively), while for Co-45Ta it was obtained a smaller value of 98,72 kJ/mol. The oxidation morphologies of Co-15Ta and Co-30Ta alloys are very similar. An external scale of Co₃O₄ characterizes them for 600 and 650°C and a duplex Co₃O₄/CoO scale for 700, 750 and 800°C, accompanied by an internal oxidation zone (IOZ), in which both metallic phases suffered oxidation. The Co-45Ta alloy displayed a different morphology characterized by the presence of an external monolayer for all oxidized coupons. At 600, 650 and 700°C the monolayer is CoO, whilst at 750 and 800°C this is Co₃O₄. Beyond the monolayers, the coupons of Co-45Ta oxidized at temperatures higher than 700°C presents a zone of internal oxidation in which only the Ta-rich phase was oxidized.

Keywords: Co-Ta, two-phase alloys, high-temperature oxidation, internal oxidation

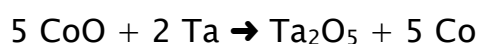
Introduction

Refractory metals bearing alloys have been considered as candidate materials for high-temperature sulphur containing atmospheres. Alloys containing Mo and Nb have been tested for this purpose^(1,2). Alloys containing Ta, in particular Co-Ta alloys, also have

been considered for this purpose, but so far only their resistance in oxygen bearing atmospheres has been evaluated.

The oxidation of binary Co-Ta alloys (10 and 15wt.%Ta) as well as of the same alloys containing carbon (up to 1wt.%C) was investigated by El-Dahshan and Hazzaa⁽³⁾ in pure oxygen and in air, at temperatures ranging from 900°C to 1100°C. They found that Ta additions reduce the oxidation rate of Co more efficiently than Cr additions. The oxidized alloys exhibit an external monolayer of CoO and a multi-phase porous internal layer composed of CoO, Ta₂O₅ and CoTaO₄. The beneficial effect of Ta was attributed to the formation of CoTaO₄, which would be responsible for the reduction of oxygen activity at metal/oxide interface, blocking its inward diffusion.

Voitovich⁽⁴⁾ *apud* El-Dahshan and Hazzaa⁽³⁾ investigated similar alloys and concluded that the positive effect of Ta is due to the removal of CoO (which presents high concentration of cationic defects) from the external layer through the following reaction:



The present investigation is part of a broader study of high-temperature oxidation resistance of refractory metals bearing alloys in different oxygen and sulphur containing atmospheres⁽⁵⁾. Its aim was to obtain further information on Co-Ta alloys behaviour in high-temperature air atmosphere so as to better understand the oxidation mechanism of these two-phase materials. In the original investigation Co-Ta alloys were oxidized only at 600°C, 700°C and 800°C⁽⁶⁾. The intermediate temperatures of 650°C and 750°C were included in the original study in an attempt to obtain two extras experimental points for the sketch of Arrhenius plots. It was not paid much attention on the morphologies of these new coupons, which are expected to be similar to at least one of the neighbor temperatures produced coupons.

Experimental

Three Co-Ta alloys, containing about 15, 30 and 45wt.%Ta (Co-15Ta, Co-30Ta and Co-45Ta, respectively), were prepared by repeatedly arc-melting appropriate amounts of the two pure metals (99.5%Co and 99.8%Ta) on a water-cooled copper hearth under high-

purity Ti-gettered argon. After cooling, the alloys were annealed under argon atmosphere at 900°C for 48 hours.

The microstructure of the three alloys is always formed by a cobalt rich phase with maximum Ta content equivalent to 3wt.% (ϵ Co) and the intermetallic phase Co_3Ta (λ_3). This microstructure does not agree with the phase diagram for Co-Ta system, shown in Figure 1⁽⁷⁾, which forecasts the formation of the peritectoid phase. This peritectoid phase, Co_7Ta_2 , has not been detected neither by XRD nor EDS. The absence of this phase is probably a consequence of the slow kinetics of the peritectoid reaction, which normally needs controlled cooling or special long-term heat treatments to allow the formation of its product. A detailed analysis of Co-Ta alloys microstructures is presented elsewhere⁽⁸⁾.

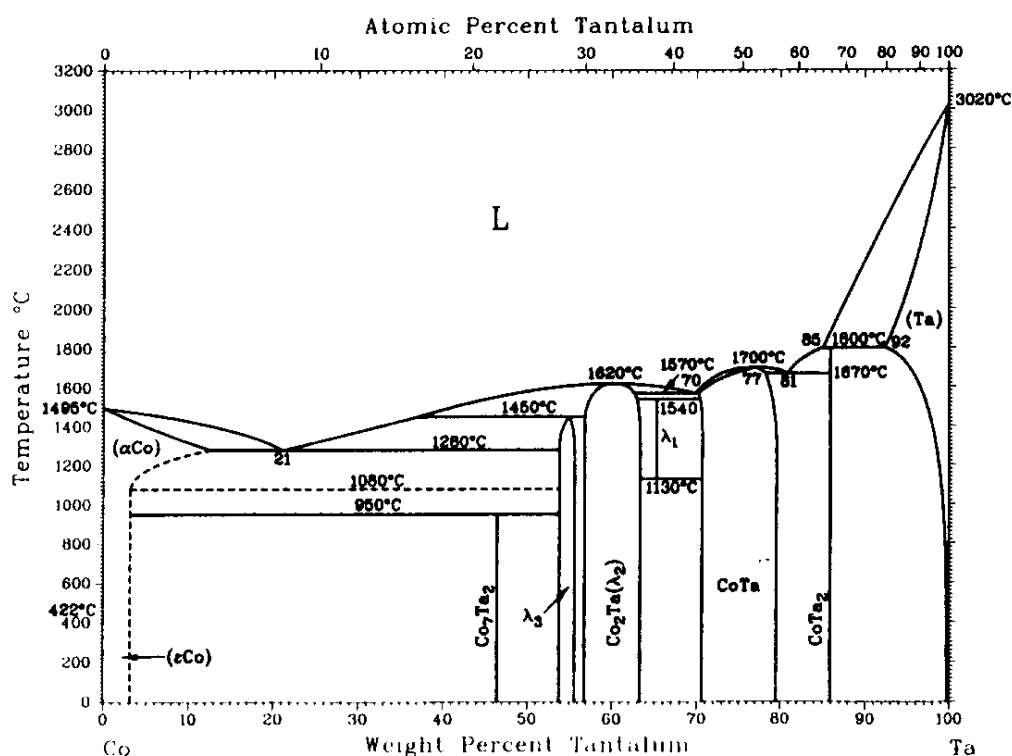


Fig. 1 – Co-Ta equilibrium phase diagram⁽⁷⁾.

Coupons of about 1,0 mm thick and with a surface area of around 2,0 cm² were cut from the ingots using a diamond-wheel saw. Coupons were ground down to 600-grit paper, cleaned with ethanol, ultrasonically rinsed in acetone and dried immediately before use.

The isothermal oxidation tests were carried out at 600°C, 650°C, 700°C, 750°C and 800°C for periods of 18 hours, at a SHIMADZU TGA-51H thermobalance with continuous weight-gain measurements. Oxidized coupons were examined by means of X-ray diffraction (XRD) for phase identification. Subsequently they were mounted in epoxy resin for transverse section examination at scanning electron microscope (SEM) and microanalysis with the energy dispersive spectrometer (EDS) X-ray attachment to the SEM, in order to identify the phases and to determine the element distribution in oxide scales.

Results

Kinetics from TGA information: The kinetics curves together with their parabolic plots are shown in Figs. 2 to 4. All coupons, except Co-45Ta alloy tested at 800°C, oxidize following the parabolic rate law. The obtained parabolic coefficients (k_p 's) as well as r-squared correlation coefficient, r^2 , of the straight lines fitted to the weight gain curves are reported in Table 1. The k_p 's were used to draw Arrhenius plots of each alloy (Fig. 5), which allowed the calculation of activation energies (Q_p 's), listed in Table 2. The alloy Co-45Ta oxidized at 800°C does not follow the parabolic rate law, what can be seen from the poor alignment of fitted straight line shown in Fig. 6. In fact, di-log plot of the kinetics presented by this coupon (not showed) revealed a slope of 0.8, confirming a behaviour intermediate between linear and parabolic.

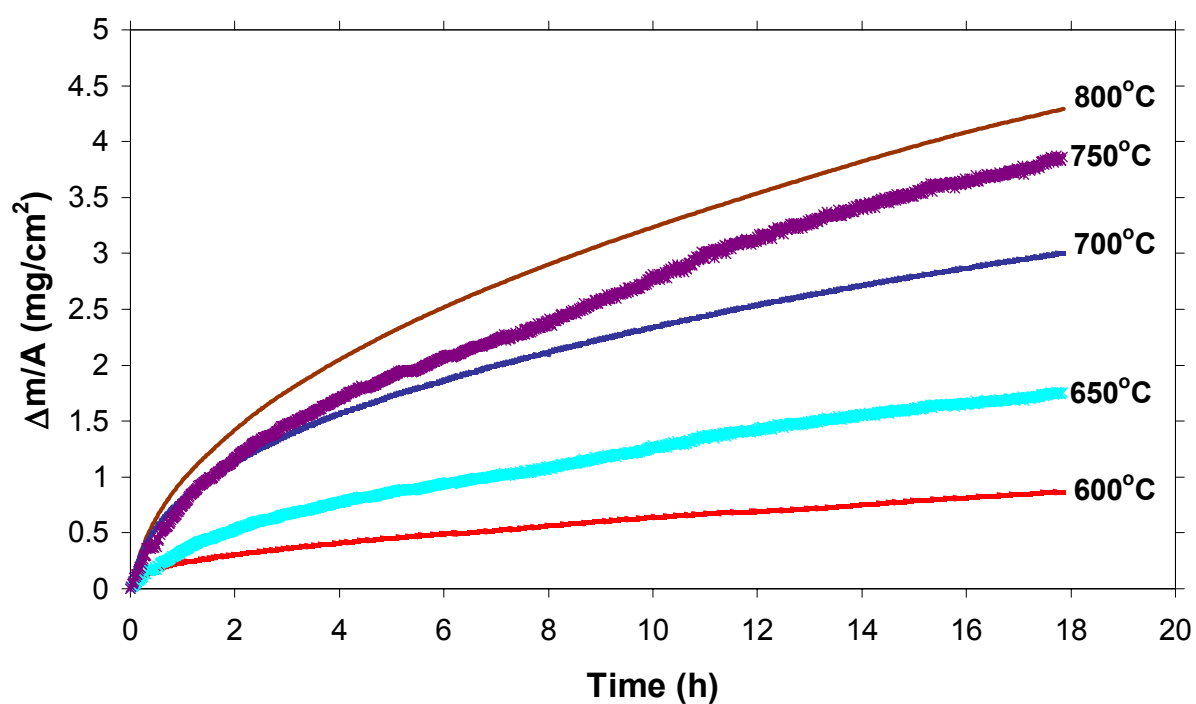


Fig. 2 – Kinetics curves for the air oxidation of Co-15Ta alloy at 600, 650, 700, 750 and 800°C.

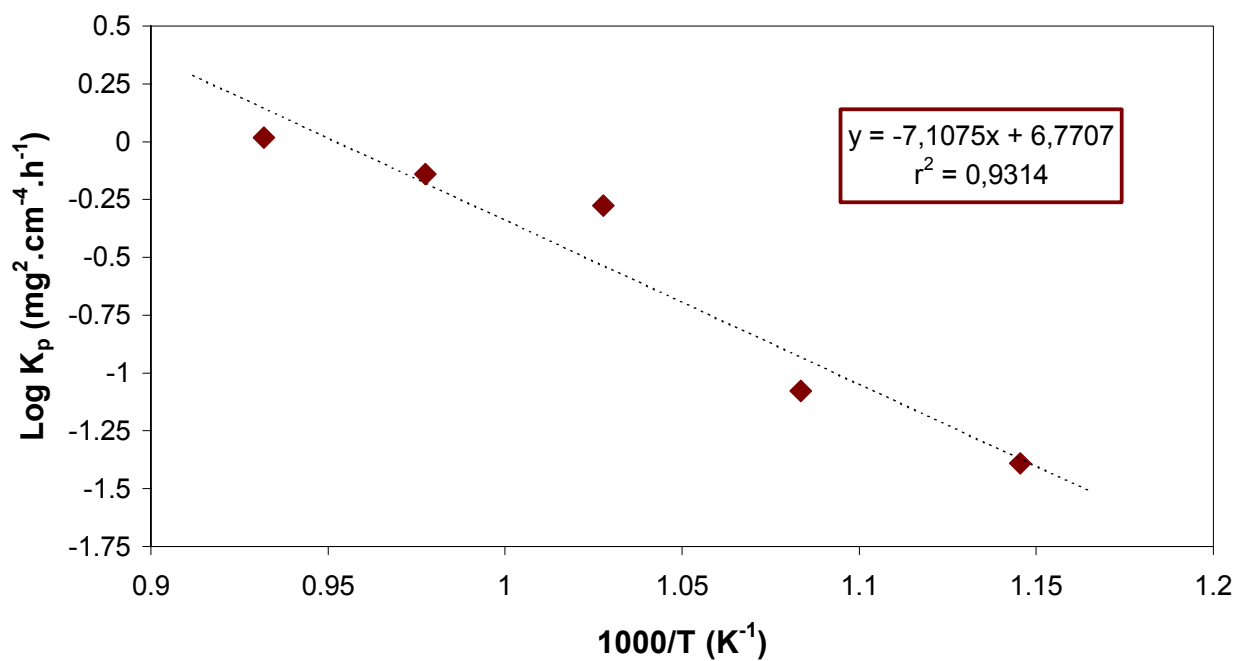


Fig. 3 – Arrhenius plots of the parabolic kinetics curves of Co-15Ta alloys, oxidized in air at 600, 650, 700, 750 and 800°C.

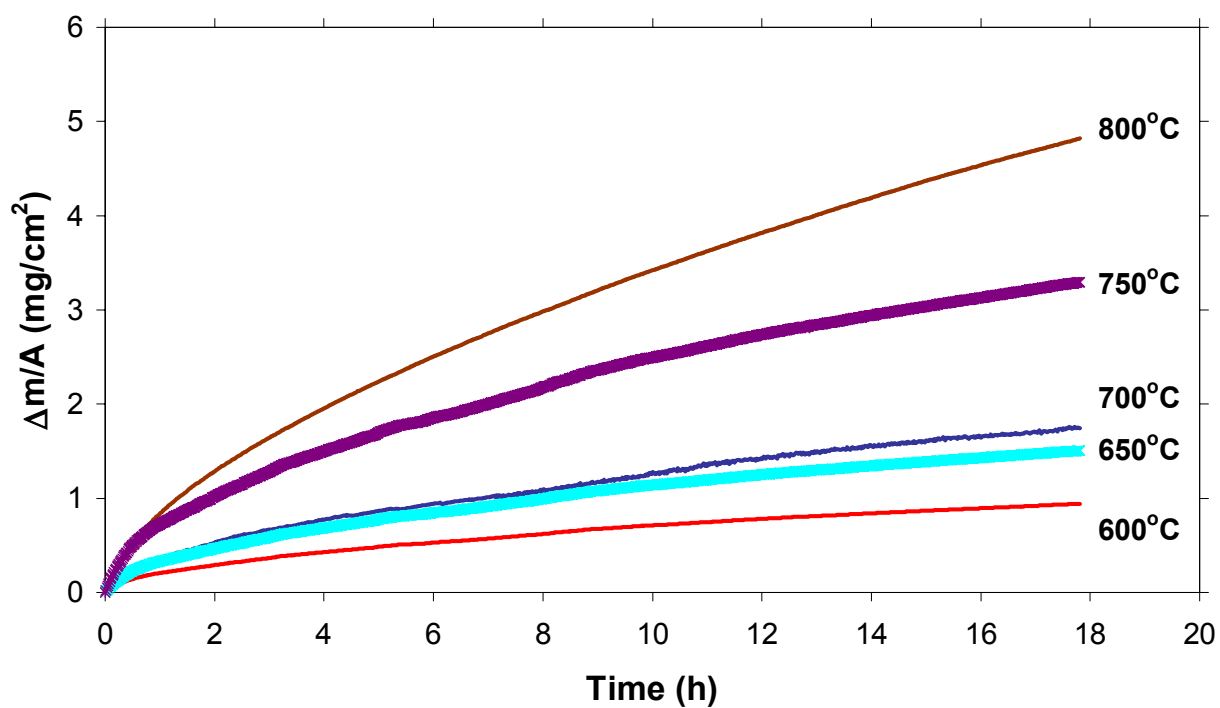


Fig. 4 – Kinetics curves for the air oxidation of Co-30Ta alloy at 600, 650, 700, 750 and 800°C.

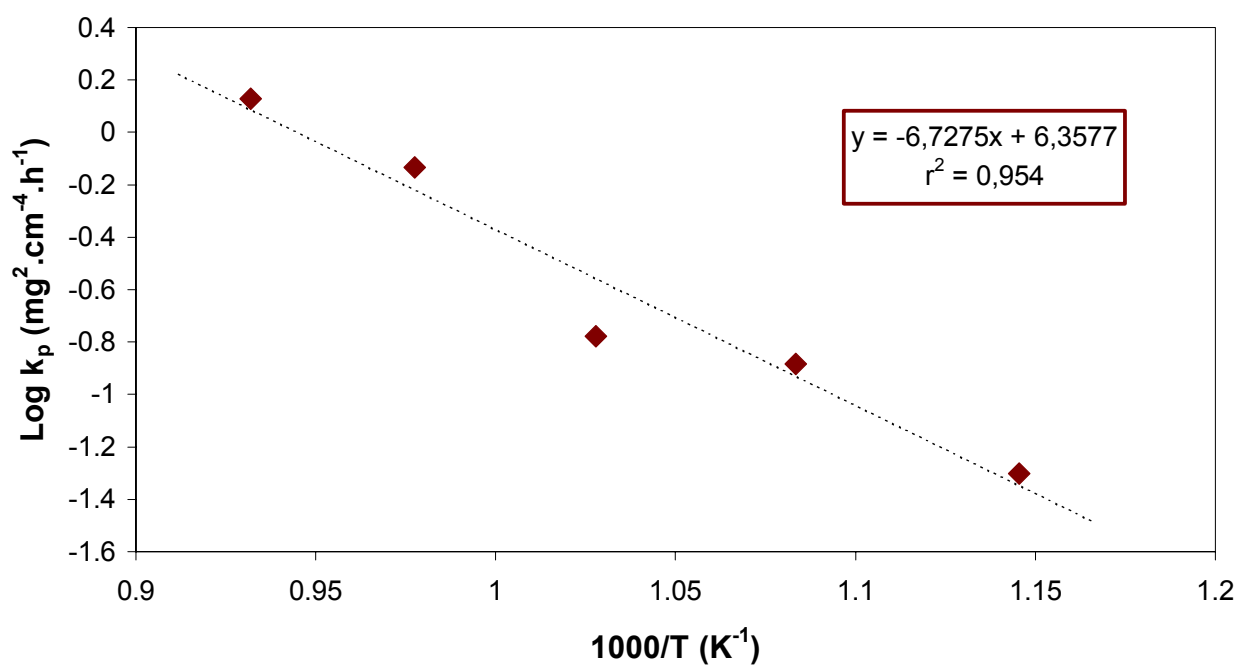


Fig. 5 - Arrhenius plots of the parabolic kinetics curves of Co-30Ta alloys, oxidized in air at 600, 650, 700, 750 and 800°C.

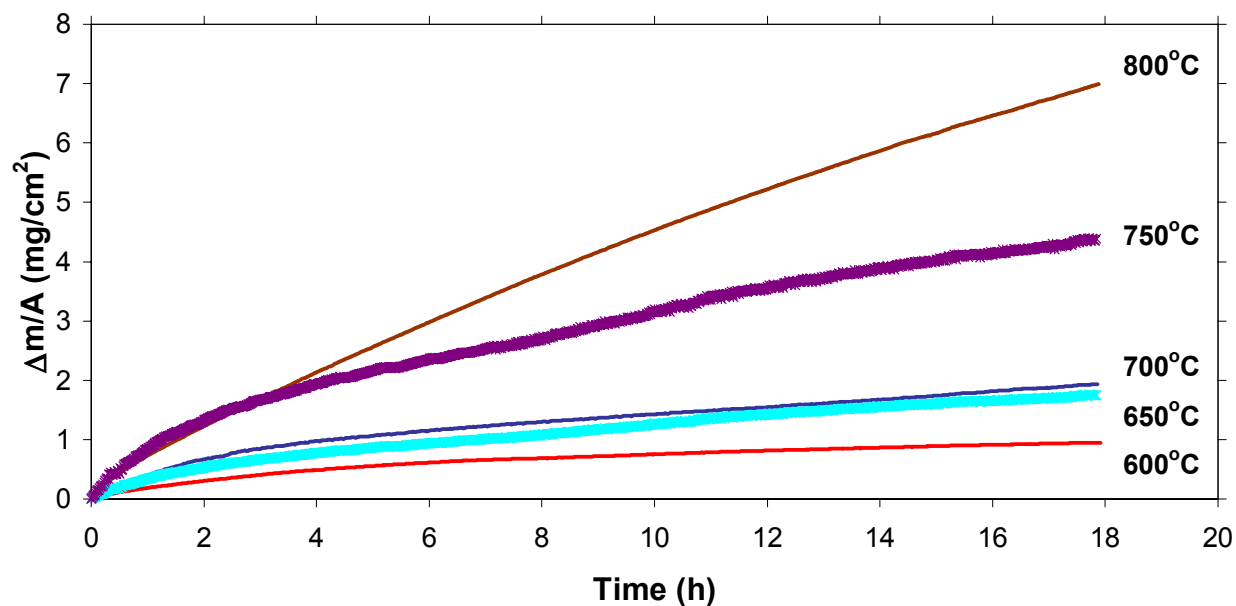


Fig. 6 - Kinetics curves for the air oxidation of Co-45Ta alloy at 600, 650, 700, 750 and 800°C.

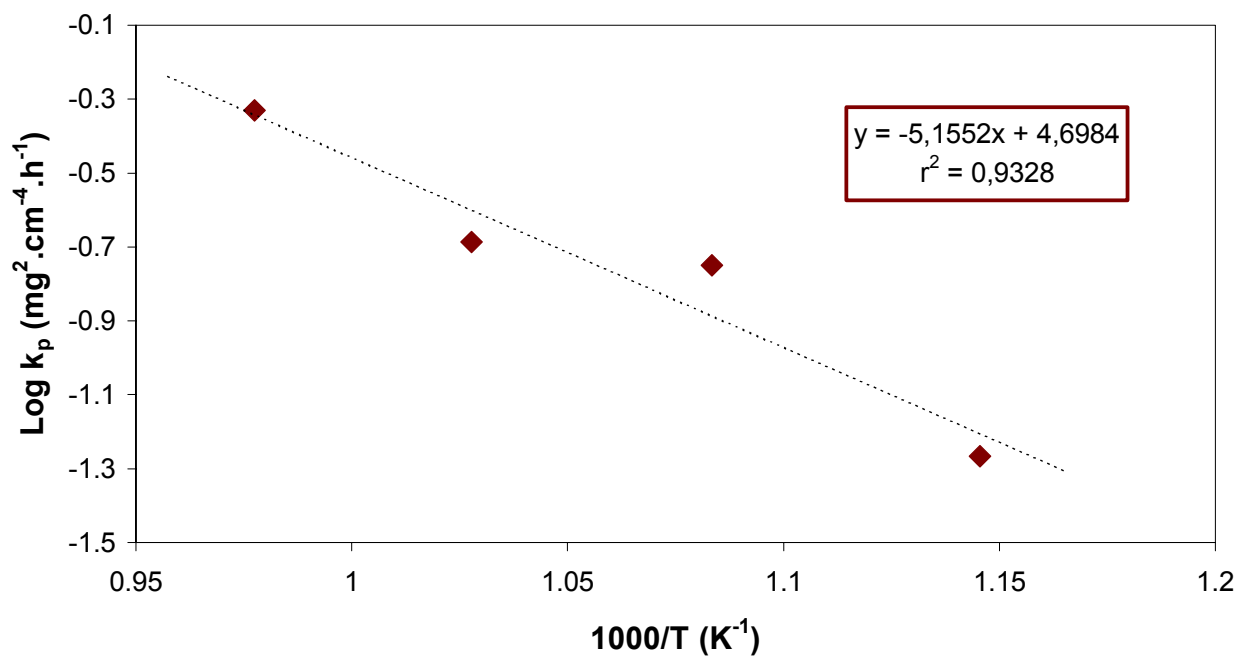


Fig. 7 – Arrhenius plots of the parabolic kinetics curves of Co–45Ta alloys, oxidized in air at 600, 650, 700 and 750°C.

Table 1 – Parabolic coefficients – k_p 's ($\text{mg}^2.\text{cm}^{-4}.\text{h}^{-1}$) – and correlation factor (r^2) of the fitted straight lines to the parabolic plots.

	Co–15Ta		Co–30Ta		Co–45Ta	
	k_p	r^2	k_p	r^2	k_p	r^2
600°C	0.04	0.99	0.05	0.99	0.05	0.99
650°C	0.08	0.97	0.13	0.97	0.18	0.97
700°C	0.53	0.99	0.17	0.99	0.21	0.99
750°C	0.72	0.99	0.73	0.96	0.47	0.96
800°C	1.04	0.99	1.35	0.99	Non-parabolic	

Table 2 – Activation energies – Q_p 's (kJ/mol) – of the alloys Co–15Ta, Co–30Ta and Co45Ta oxidized in air, at 600, 650, 700, 750 and 800°C (for Co–45Ta alloy, non-parabolic kinetics at the highest test temperature). The correlation factors (r^2) are also shown.

	Co–15Ta	Co–30Ta	Co–45Ta
Q_p	136.11	128.83	98.72
r^2	0.93	0.95	0.93

Scale Structure and Composition: The alloys Co–15Ta and Co–30Ta oxidized at the same temperature produced very similar morphologies. Test coupons oxidized at 600°C and 650°C develop a monolayer of Co_3O_4 (see Fig. 8), while at the three highest temperatures duplex scales are formed with Co_3O_4 being the outermost and CoO the innermost layer, as shown in Figs. 9 and 10. The internal scales have a two-phase microstructure, resembling that of the alloys, i.e, the spatial distribution of the oxide phases is exactly the same as that at the metallic phases present in the alloys before its oxidation (see Figs. 9 and 10). The EDS analysis has shown that both metallic phases of the alloys were oxidized, being this type of oxidation known as heterophasic region – HR. The stoichiometric analysis of HR showed that the cobalt-rich phase was transformed to CoO, while the intermetallic phase was converted to the double oxide $\text{Co}_4\text{Ta}_2\text{O}_9$ for the Co–15Ta alloy and CoTaO_4 for the Co–30Ta alloy. The XRD analysis of Co–15Ta alloys detected CoTa_2O_6 in the coupons oxidized

at 600°C and 650°C and this double oxide together with $\text{Co}_4\text{Ta}_2\text{O}_9$ in the three other coupons, whilst for all Co-30Ta coupons no double oxides were detected. These different data supplied by EDS and XRD may indicate that, instead of double oxides, tantalum-rich phase could have formed a mixture of Ta_2O_5 plus either CoO or metallic Co, at least in the coupons which fail to reveal the presence of double oxides when analyzed by XRD.

All Co-45Ta coupons displayed an external monolayer (see Figs. 11 and 12), in a way similar to that of Co-15Ta tested at the two lowest temperatures. For coupons oxidized at 600°C, 650°C and 700°C the EDS analysis indicated that this monolayer is CoO, while for the coupons oxidized at the two higher temperatures this monolayer is Co_3O_4 . The formation of these two cobalt oxides was confirmed by XRD analysis. Moreover, the oxidation at 750°C and 800°C produced a thick internal oxidation zone (particularly for the highest temperature = 57 μm) (see Fig. 12), which is also observed on the coupon oxidized at 700°C, but very thin (5 μm) (see Fig. 11). The morphology of this internal scale is different from that observed on Co-15Ta and Co-30Ta alloys, indicating that only the intermetallic phase was internally oxidized in the Co-45Ta alloy, i.e., an internal oxidation zone – IOZ. However, in a similar way to these alloys, the internal scale of Co-45Ta alloy shows no spatial distribution difference when compared to the metallic alloy.

The XRD analysis of oxidized Co-45Ta specimens detected some nitrogen-containing phases: tantalum nitrides (TaN , Ta_2N and Ta_4N) and $\text{Co}(\text{NO}_3)_2$. These phases were not identified in the scales because EDS microprobe was used to analyze only Co, Ta and O.

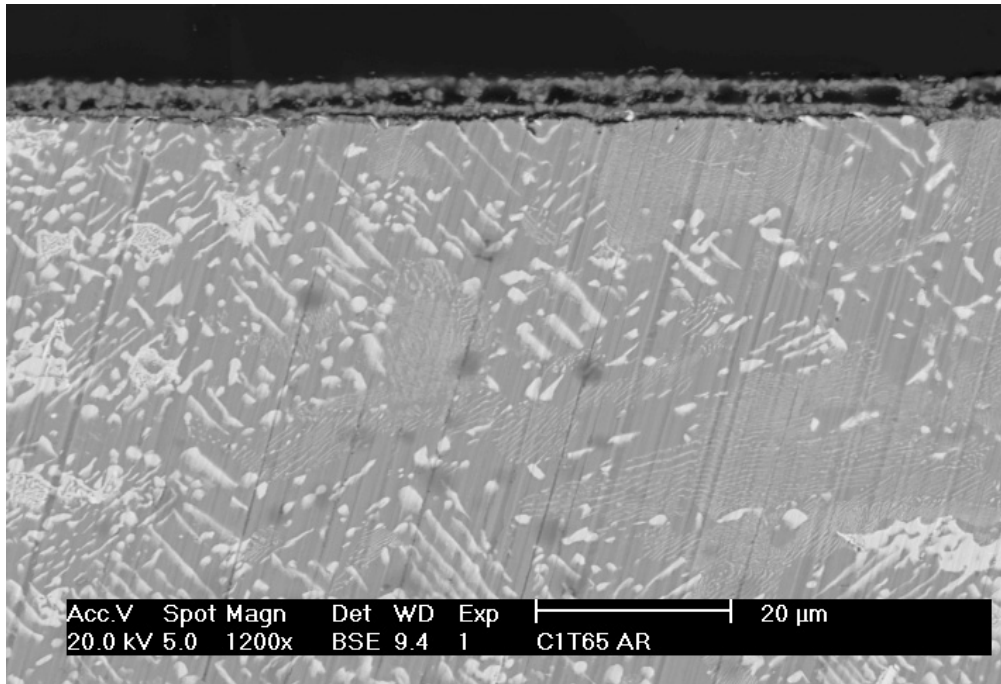


Fig. 8 – Cross section (BSE) of Co-15Ta alloy oxidized at 650°C in air for 18 hours, where it is possible to observe an external monolayer and no attack in the underlying alloy.

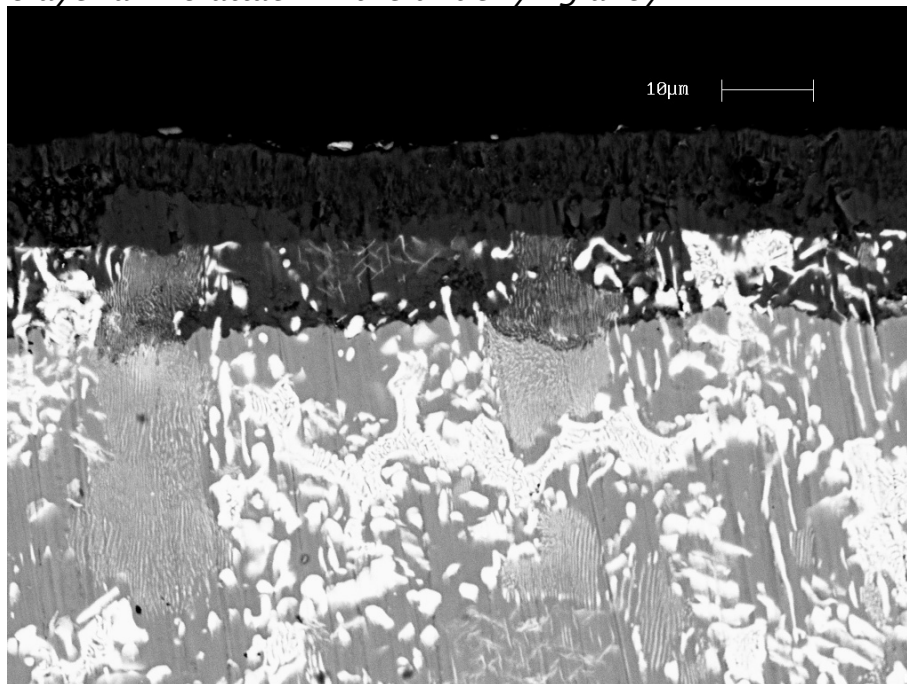


Fig. 9 – Cross section (BSE) of Co-15Ta alloy oxidized at 700°C in air for 18 hours, which shows the formation of a duplex external scale (#1 outermost – Co_3O_4 and #2 innermost – CoO), together with an HR (#3 and #4) of both oxidized original metallic phases. #5 and #6 are the metallic phases.

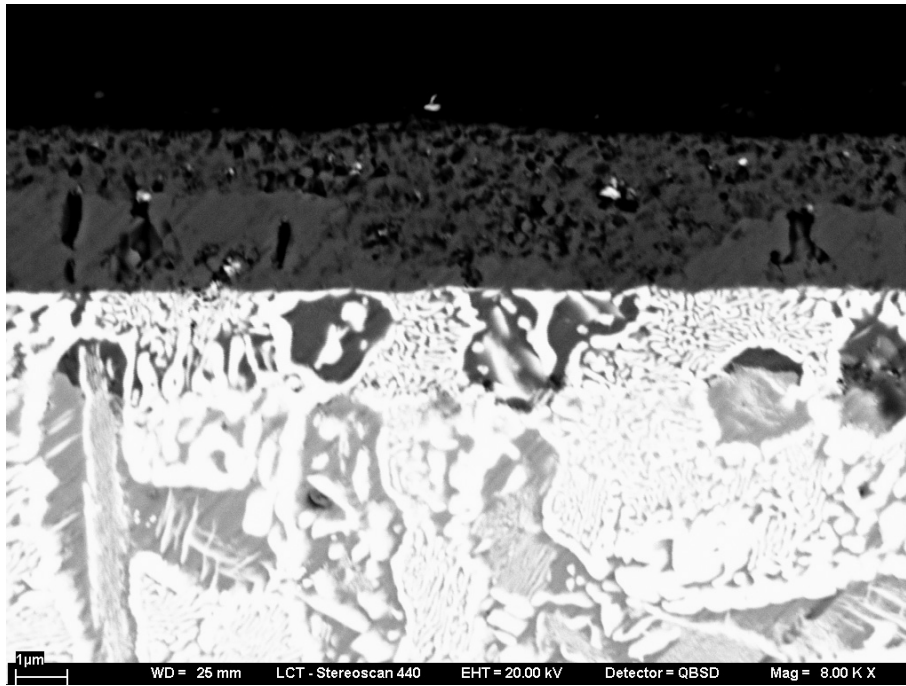


Fig. 10 – Cross section (BSE) of Co-30Ta alloy oxidized at 750°C in air for 18 hours, which repeated the morphology shown in Fig. 9, i.e., an duplex $\text{Co}_3\text{O}_4/\text{CoO}$ external scale, together with an HR of both oxidized original metallic phases.

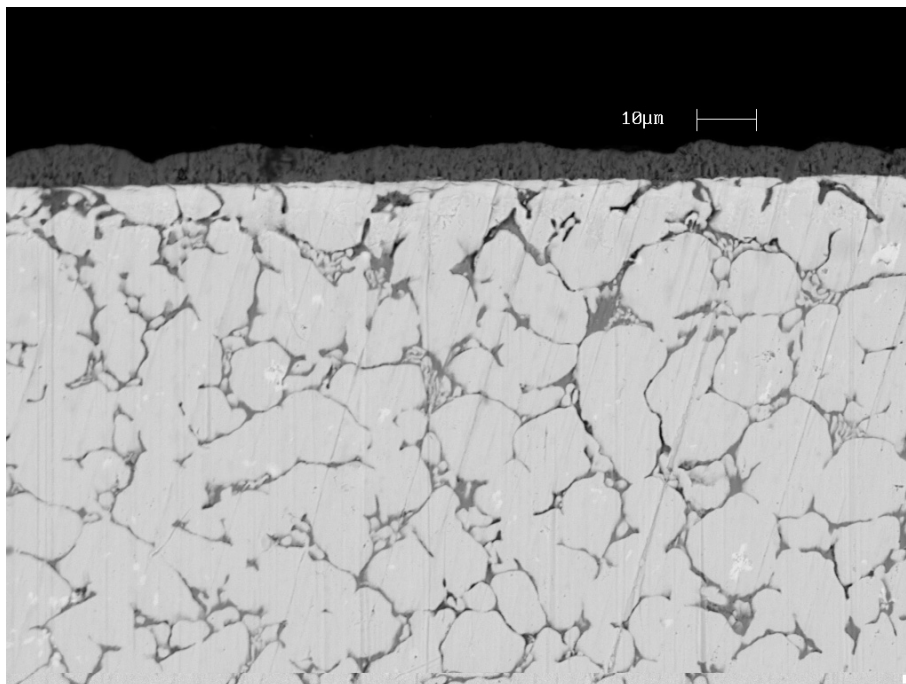


Fig. 11 – Cross section (BSE) of Co-45Ta alloy oxidized at 700°C in air for 18 hours, showing the formation of an external Co_3O_4 monolayer and a thin IOZ of approximately 5

μm (better noted at higher magnifications), where only the Ta-rich phase is oxidized.

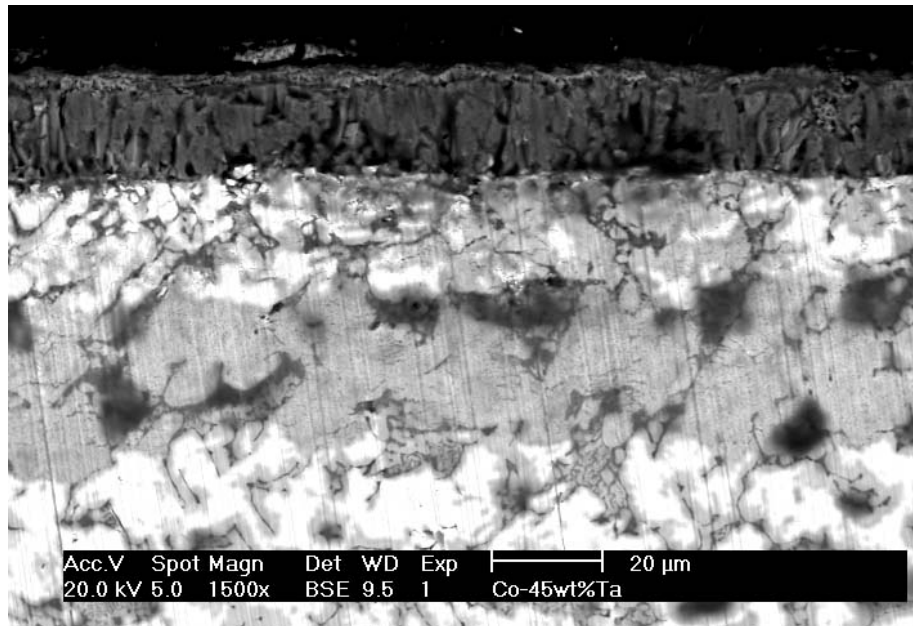


Fig. 12 – Cross section (BSE) of Co-45Ta alloy oxidized at 800°C in air for 18 hours. Similarly to the oxidation at 700°C (Fig. 11) this coupon develop an external Co_3O_4 monolayer and a rather thick IOZ of 40 μm , where only the Ta-rich phase is oxidized.

Kinetics from total scale thickness: In order to allow the determination of the oxidation kinetics from the measurement of scale thickness, it was first tried to compare the thickness of the different observed layers. For the reason of the large morphological variance among the tested coupons, it was not possible to establish the comparison as originally though. The only way to do the scale thickness' comparison is to consider the total scale of each tested coupon. Table 3 lists the total scale thickness (t) of all tested coupons. Based on these, Arrhenius plots are drawn for each alloy (Figs. 13 to 15), which allow the calculation of the oxidation energy activation derived from scale thickness – Q_t . Table 4 lists Q_t 's values and the obtained correlation coefficient r^2 .

Table 3 – Average total scale thickness – t (μm) of Co-Ta alloys, oxidized in air at 600, 650, 700, 750 and 800°C, for 18 hours.

	Co-15Ta	Co-30Ta	Co-45Ta
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	<i>t</i>	<i>t</i>	<i>t</i>
600°C	3.8	7	4.3
650°C	6	11	7.5
700°C	20.8	13	11
750°C	28.5	38.7	40.5
800°C	39.3	55.6	58.6

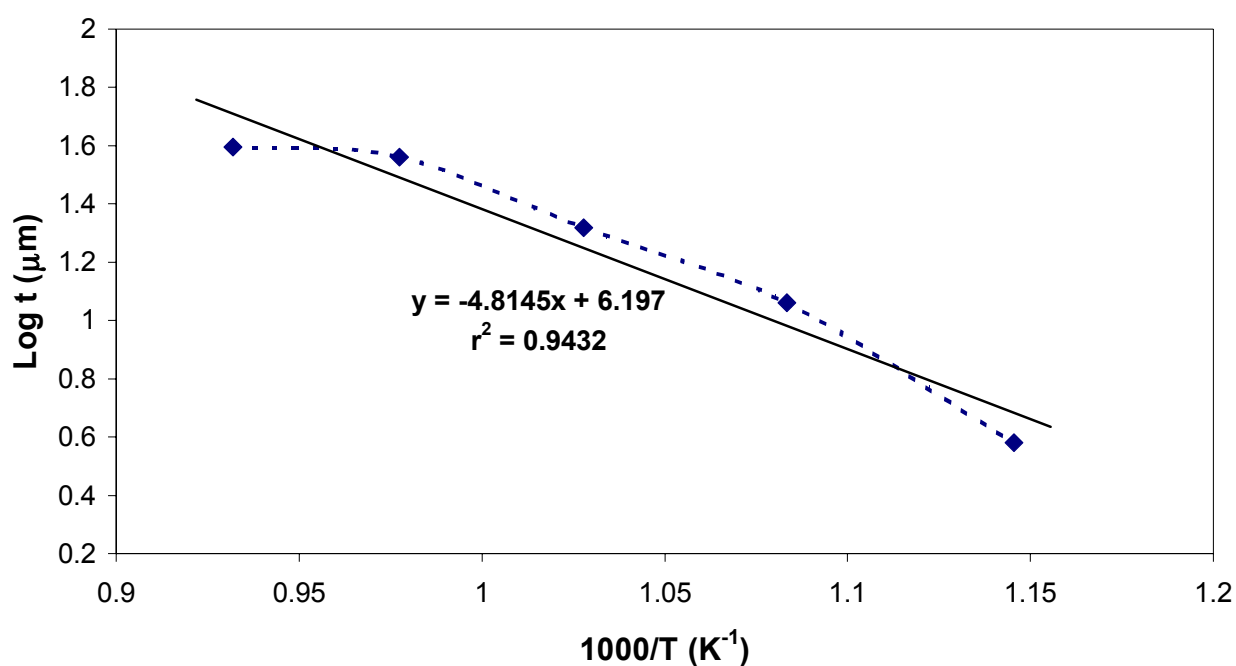


Fig. 13 - Arrhenius plot of the total scale thickness of Co-15Ta alloy, oxidized at 600, 650, 700, 750 and 800°C.

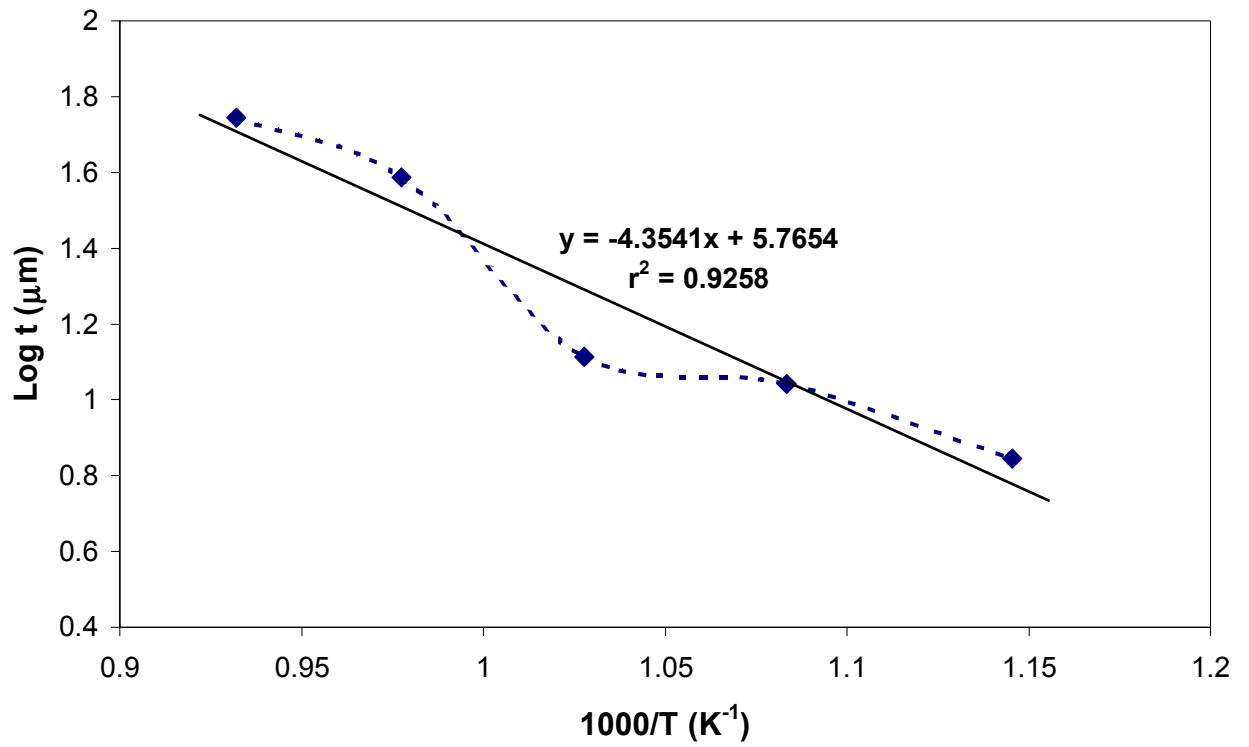


Fig. 14 - Arrhenius plot of the total scale thickness of Co-30Ta alloy, oxidized at 600, 650, 700, 750 and 800°C.

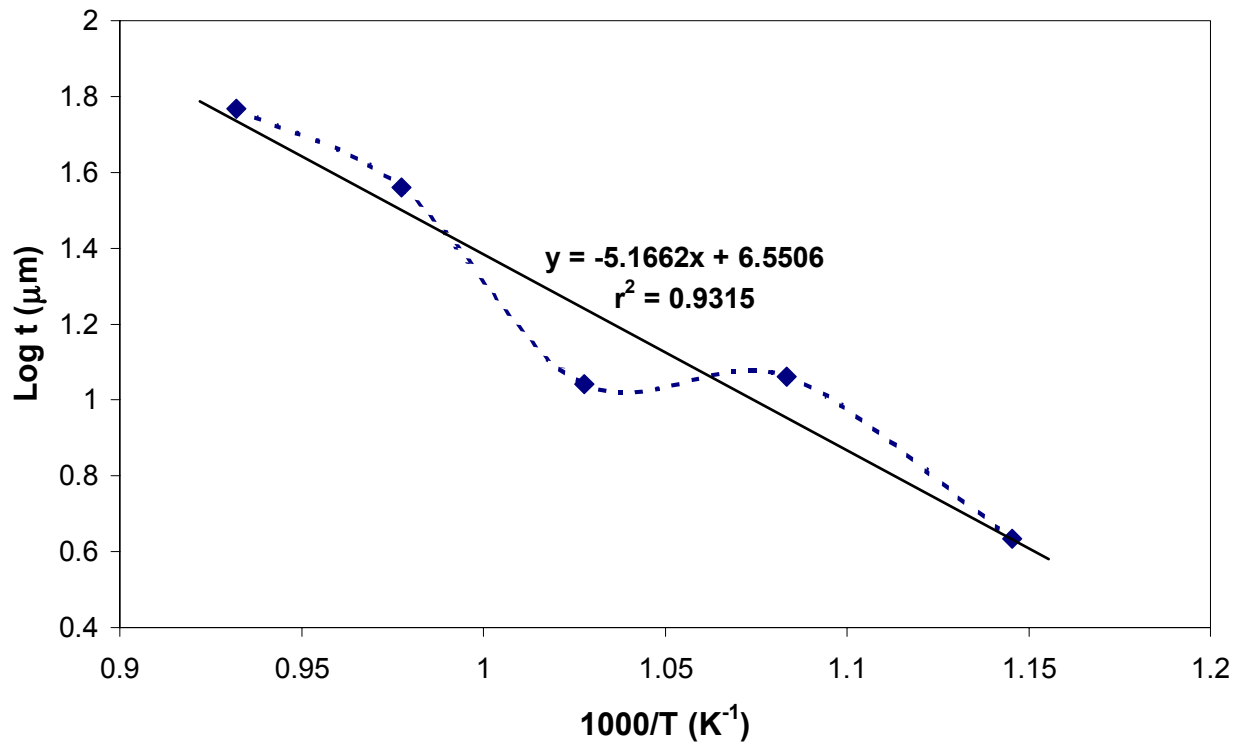


Fig. 15 - Arrhenius plot of the total scale thickness of Co-45Ta alloy, oxidized at 600, 650, 700, 750 and 800°C.

Table 4 – Activation energies calculated from the average total scale thickness – Q_t 's (kJ/mol) – of the alloys Co-15Ta, Co-30Ta and Co-45Ta oxidized in air, at 600, 650, 700, 750 and 800°C. The correlation factors (r^2) are also shown. In the last row it is listed the relation Q_p/Q_t (see Table 2).

	Co-15Ta	Co-30Ta	Co-45Ta
Q_t	92.20	83.38	98.93
r^2	0.93	0.95	0.93
Q_p/Q_t	1.476	1.545	0.998

Discussion

As was already stated there is a significant difference in oxidized scale morphology between the Co-15Ta and Co-30Ta alloys and the Co-45Ta alloy. The main difference is the type of internal oxidation that was formed in these alloys, since in the latter only the Ta-rich phase is oxidized.

When no metallic diffusion occurs and only one alloy element is oxidized by the inward diffusion of oxygen this type of internal oxidation of two-phase alloys is called “diffusionless” or “in situ” or “in place” internal oxidation^(9,10). The inward oxygen diffusion causes a progressive drop of oxygen partial pressure. At a certain depth the oxygen partial pressure is not sufficient to oxidize Co but can still oxidize Ta, since the latter is more reactive (less noble) than Co.

In the internal oxidation zone (IOZ) of alloys Co-15Ta and Co-30Ta both metallic phases were oxidized. This implies that the oxygen partial pressure at the reaction front is higher than the dissociation pressure of CoO. This type of internal oxidation may also produce another more internally located IOZ. This second IOZ is characterized by a morphology in which only the phase that contains the most reactive element is oxidized such as the one observed in Co-45Ta alloy. Nevertheless, this second IOZ was formed in neither Co-15Ta nor Co-30Ta alloys. The absence of this second IOZ is an indication of a possible obstruction of oxygen by the actual IOZ. This obstruction is certainly related to the nature of the oxidation products of this layer, which suppress oxygen diffusion through the first IOZ.

Another factor, which could have contributed to the different type of internal oxidation shown by Co-45Ta alloy, is the volume fraction of Ta rich phase (λ_3), which is approximately 90%. Even if oxygen partial pressure is sufficient to oxidize Co, the much bigger λ_3 -volume fraction determines a greater possibility for oxygen to meet Ta than Co. Moreover, there is also the kinetics factor. If the growing rate of Ta oxides is greater than that of Co oxides (what is normally observed at conditions of high oxygen pressure), then Ta oxides may grow and coalesce, isolating Co rich phase from oxygen attack. For this mechanism to be operative there is a need of a minimum volume fraction of λ_3 , i.e., there must be a critical volume fraction of Ta rich phase to suppress the oxidation of Co. This critical λ_3 -volume fraction seems to be between that found in Co-30Ta alloy (IOZ characterized by the oxidation of both metallic phases) and Co-45Ta alloy (only λ_3 oxidizes).

The oxidation kinetics of Co-45Ta alloy at 800°C was found to be intermediate between linear and parabolic (slope of 0,8 on the di-log plot). This result reveals the greater aggressiveness of corrosion of Co-45Ta at 800°C when compared to the other test temperatures. A comparison of Co-45Ta coupons oxidized at 700°C and at the two highest test temperatures (750 and 800°C) points out a considerable morphological difference between them, both for external and internal scales. At the lower temperature the external monolayer is essentially CoO whilst at the two highest temperatures it is Co₃O₄. Nevertheless it is not believed that only this difference should impose such distinct kinetics behaviour. A striking difference is also observed between the IOZ's; while for the coupon oxidized at 700°C it is only 5 μm thick, for the coupon oxidized at 800°C it is 42 μm thick. This large difference cannot be explained only in terms of different test temperatures, even though one assumes that the IOZ growing is controlled by inward diffusion of oxygen, which is a thermally activated process. It seems to be more reasonable to connect the more aggressive kinetics at 800°C to the nature of the external monolayer. Co-45Ta oxidized at 750°C followed the parabolic rate law in spite of being showed the same morphology of the alloy after oxidation at 800°C. This information could be interpreted as being contradictory, since it was expected for these two oxidation temperatures to produce

similar kinetics, in agreement to the observed similar morphologies. Nevertheless a careful examination of the Co-45Ta oxidation kinetics' reveal that the parabola obtained at the temperature of 750°C has a k_p with is more than the double of the one for 700°C. Apparently, the oxygen diffusion through Co_3O_4 is much easier than through CoO . This conclusion is supported also by the fact that for 750°C and 800°C coupons the thickness of external layers are 13.5 and 16.6 μm , respectively, while for 700°C coupon it is only 6.3 μm .

The literature data⁽¹¹⁾ states that the oxygen diffusion coefficient in Co_3O_4 is $2.4 \times 10^{22} \exp(-736(\text{kJ/mol})/\text{RT}) \text{ m}^2/\text{s}$ while in CoO it is $8.8 \times 10^{-4} \exp(-287(\text{kJ/mol})/\text{RT}) \text{ m}^2/\text{s}$. This data for CoO was determined in the range of 1,050°C to 1,300°C, while for Co_3O_4 there is no information as to the temperature range in which it is valid. However, if we assume that these values are valid at 800°C, then the oxygen diffusion coefficients for Co_3O_4 and CoO would be $3.56 \times 10^{-14} \text{ m}^2/\text{s}$ and $9.41 \times 10^{-18} \text{ m}^2/\text{s}$, respectively. This is in agreement with the above finding.

The reasons for Co_3O_4 monolayer formation on Co-45Ta alloy at 750°C and 800°C in substitution of CoO monolayer formed at lower temperatures require more investigation. This study should take into consideration the Ta doping effects on cobalt oxides.

The obtained activation energy calculated from the mass-gain data (Q_p) for each studied alloys (Table 2) shows smaller values for progressively more Ta concentrated alloys, which means that the higher the Ta content the less sensitive to temperature is the alloy. The same analysis based on the activation energies calculated from the average total scale thickness (Q_t 's) was not possible, due to the lack of a bias, as shown in Table 4.

The activation energies calculated from the mass-gain data (Q_p 's) of Co-15Ta and Co-30Ta alloys are close and their activation energies calculated from the average total scale thickness (Q_t 's) is reasonably close and about 33% smaller than Q_p 's. These results are in agreement with the morphological similarities displayed by the considered alloys when oxidized at the same temperatures. Although at the highest temperature Co-45Ta showed non-parabolic kinetics, the activation energy (Q_p) was calculated based on the other four test

temperatures and revealed a significantly smaller value compared to the two other alloys. The calculation of Q_t for Co-45Ta alloy led to a value extremely close to Q_p , which is only 0.02% smaller than Q_t , according to Table 4.

The observed similarities between Q_p and Q_t for Co-45Ta must be related to the nature of its internal scale, which is an IOZ. Depending on the oxidation temperature, the tested coupons formed an IOZ, which thickness corresponds to almost 70% of the total scale thickness. Differently, the HR thickness measured in Co-15Ta and Co-30Ta alloys are never thicker than the corresponding external scale (i.e., HR thickness participates of less than 50% of the total scale thickness). Although thick, the contribution of the IOZ to the mass-gain of Co-45Ta alloy is not so significant as the one of the HR experimented by Co-15Ta and Co-30Ta, since only Ta is internally oxidized.

The different nature of the internal scale formed in Co-15Ta and Co-30Ta (HR) and Co-45Ta (IOZ) determined the impossibility to correlate Q_p and Q_t in a comprehensive manner.

Conclusions

- All coupons, except the alloy Co-45Ta oxidized at 800°C, follow the parabolic rate law.
- The close activation energy values (both Q_p and Q_t) for oxidation of Co-15Ta and Co-30Ta alloys, as well as their similar morphologies, suggest the existence of a unique oxidation mechanism for these alloys.
- In the internal oxidation zone (IOZ) of Co-45Ta alloy only the Ta-rich phase suffers oxidation, while in the IOZ of the other two alloys both metallic phases are internally oxidized (HR).
- The different nature of the internal scale observed in Co-15Ta and Co-30Ta alloys (HR) in comparison to Co-45Ta (IOZ) preclude the correlation of Q_p and Q_t in a comprehensive manner.
- On Co-45Ta alloy oxidized at 600°C, 650°C and 700°C a CoO monolayer is formed, while on the alloy oxidized at 750°C and 800°C Co_3O_4 replaces this oxide. Moreover much thicker IOZ's are formed in the latters, which appears to be a consequence of the nature of their external monolayer.

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