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Oxidation resistance of ODS alloy PM2000 from 880 °C to 1400 °C

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Oxide dispersion strengthening (ODS) alloys show superior high temperature creep and oxidation resistances. Those alloys may be used in various industries where the increase of process efficiency requires enhanced high temperature performances [1]. Powder metallurgy ferritic alloy PM2000 (20 wt % chromium, 5.5 wt % aluminium, 0.5 wt % titanium) contains a small amount of finely dispersed yttria (0.5 wt %). The thermodynamically stable dispersoids retain strengthening up to much higher temperature than that achieved in conventional wrought or cast alloys. Another benefit of oxide dispersoids is to stabilize the coarse microstructure of the material characterized by elongated grains with high grain aspect ratio [2]. The outstanding oxidation resistance of ODS ferritic alloys is due to the formation of a slowly growing and well adherent alumina scale at the surface of the material during high temperature exposure. The presence of yttria dispersion has a beneficial effect on the oxidation resistance of the material. Several mechanisms have been proposed to explain the improvement of scale protective properties imparted by the presence of active elements such as yttrium [3, 4].

This letter compares the performances of alloy PM2000 exposed to air at various temperatures from 880 °C to 1400 °C in terms of oxidation kinetics and alumina scale morphology, crystal structure and composition.

Alloy PM2000 was supplied by Plansee GmbH in the shape of sheets 4 mm thick. Specimens were isothermally oxidized in air at 880 °C, 1050 °C, 1150 °C, 1230 °C and 1400 °C for periods up to 300 h. For each tested temperature, oxidized specimens, contained in crucibles, were cooled to room temperature after different exposure periods for gravimetric measurement of the extents of attack. For studies of scale morphology, composition and crystal structure, scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX), electron probe micro-analysis (EPMA) and X-ray diffraction (XRD) were used.

Gravimetric measurements showed that the kinetics of oxidation exhibit a parabolic behavior where the weight gain of specimens per unit area is proportional to the square root of the exposure time. The values of the parabolic rate constant k_p, determined from the experimental data, are given in Table I.

For temperatures ranging from 880 °C to 1400 °C, the attack of the alloy is essentially protective as the oxidation kinetics are parabolic. Fig. 1 is an Arrhenius plot of the variation of the parabolic rate constant with reciprocal temperature.

Calculated data at 1400 °C, 1230 °C, 1150 °C and 1050 °C fit a single regression line showing that the oxide growth is thermally activated with an activation energy of about 2×10^5 J mol^{-1}. At 880 °C, the growth rate is much higher than the rate extrapolated from the Arrhenius plot of Fig. 1.

Fig. 2 compares X-ray diffraction analysis of the surface scales after 240 h exposure at 880 °C, 200 h at 1050 °C, 168 h at 1150 °C, 162 h at 1230 °C and 100 h at 1400 °C. In all cases, rhombohedral α-Al_2O_3 is formed at the surface of specimens. Note the occurrence of an Fe peak on the 880 °C diffraction pattern, characteristic of the underlying matrix, due to the small thickness of the scale. At

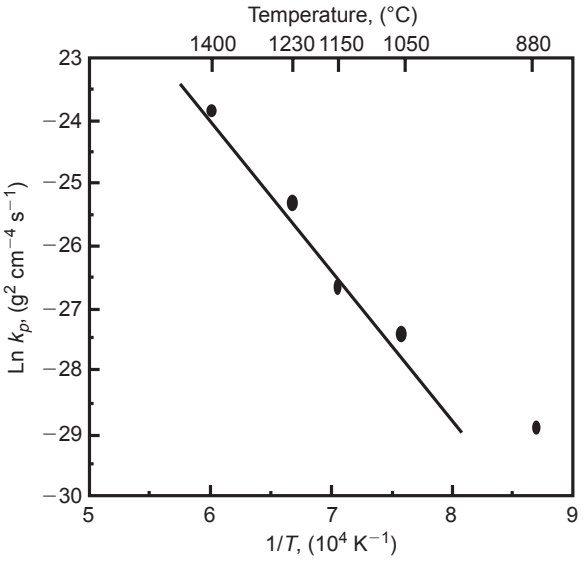


Figure 1 Arrhenius-plot of oxidation rate constant k_p versus reciprocal temperature.

TABLE I Values of the parabolic rate constant k_p

Temperature (°C)	880	1050	1150	1230	1400
k_p (g^2 cm^{-4} s^{-1})	2.77×10^{-13}	1.23×10^{-12}	2.65×10^{-12}	1.01×10^{-11}	4.50×10^{-11}

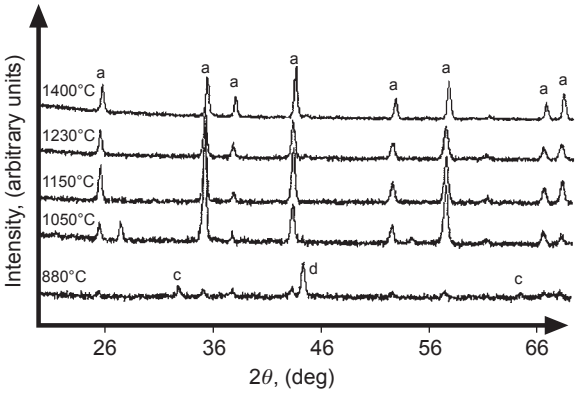


Figure 2 X-ray diffraction results (a = α-Al_2O_3, c = θ-Al_2O_3, d = Fe).

880 °C, in addition to α-Al_2O_3, X-ray diffraction reveals the presence of monoclinic θ-Al_2O_3.

Fig. 3 shows the typical morphology of the surface scale after 70 h exposure at 1150 °C. A flat base scale is formed on which small nodules are located. EDX analysis (Fig. 4) shows that the flat base scale is pure Al_2O_3 while nodules mainly contain titanium and yttrium. Such nodules are assumed to be mixed Ti/Y oxides. The aluminum peak present on the EDX pattern of the nodule is attributed to the surrounding alumina scale. This type of morphology was observed at all temperatures and for all exposure times. Only the size and density of nodules, as well as the thickness of the oxide scale, varied.

For specimens oxidized at 880 °C, the structure of the scale is no longer single phase as additional alumina particles were observed. Such a particle which exhibits a needle-like structure is shown in Fig. 5. The presence of this type of particle was correlated to the XRD analysis described previously and they were assumed to be θ-Al_2O_3.

No indication of spallation was found for temperatures in the range 880 °C–1230 °C, whereas at 1400 °C a significantly large area of the scale spalled on cooling to room temperature as discrete particles (Fig. 6). The decohesion may occur either at the oxide/matrix interface or within the oxide scale.

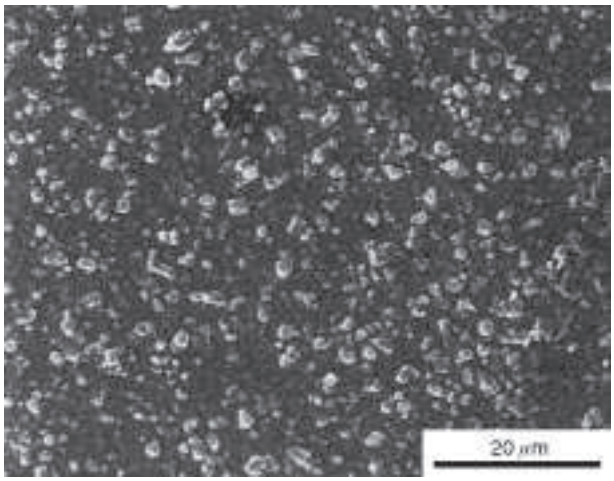


Figure 3 Scale morphology of specimen after 70 h isothermal oxidation at 1150 °C.

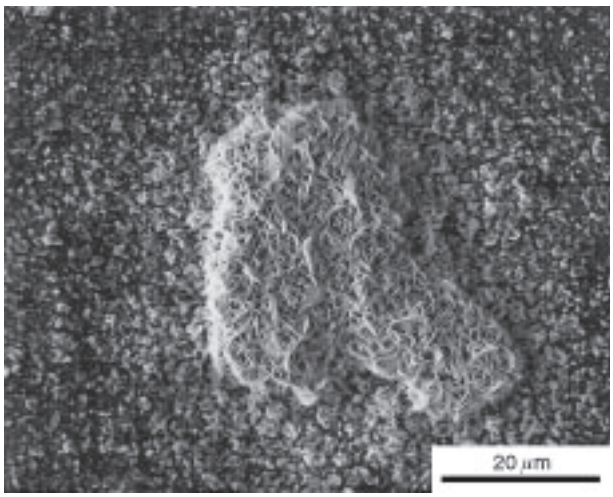


Figure 5 Scale morphology of specimen after 200 h isothermal oxidation at 880 °C.

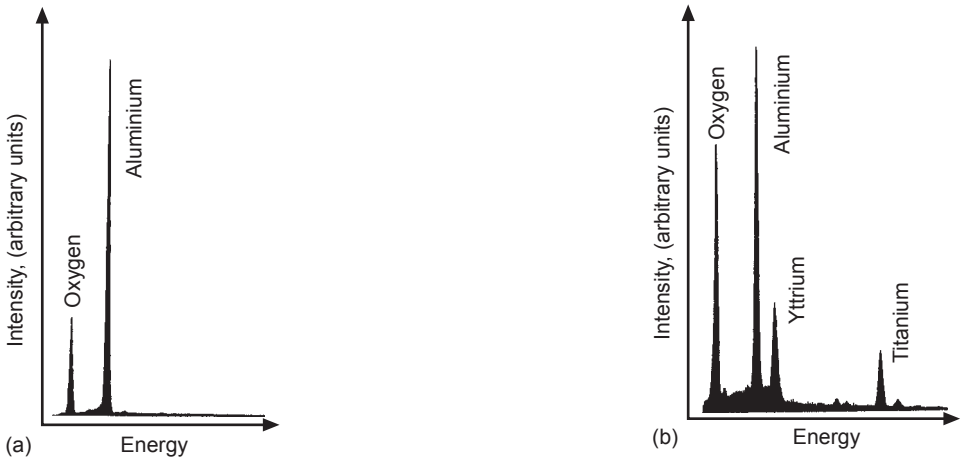


Figure 4 EDX analysis of specimen after 70 h isothermal oxidation at 1150 °C, (a) flat base scale, (b) overlying nodule.

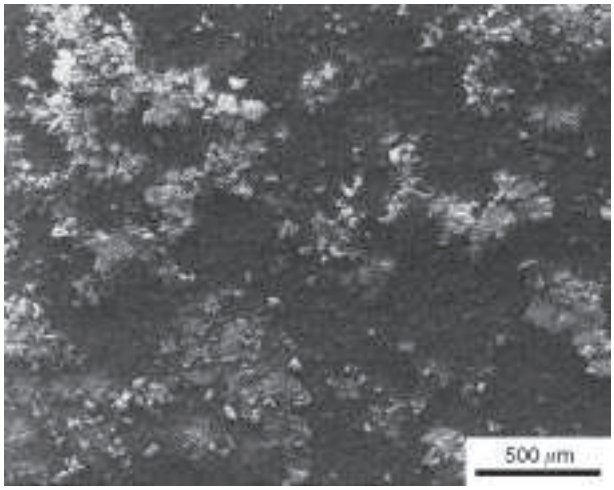


Figure 6 Scale morphology of specimen after 168 h isothermal oxidation at 1400 °C.

The elemental constituents of the oxide scales were determined by EPMA of transverse sections of all specimens. An example is shown in Fig. 7 for a specimen oxidized for 240 h at 880 °C. The examination of the oxidized section of the material reveals regions rich in titanium and yttrium within the Al_2O_3 scale.

Fig. 8a shows a micrograph of the cross-section of the oxide scale formed after 100 h exposure at 1400 °C. Within the oxide scale, note the presence of a particle with a different contrast from that of the alumina. Fig. 8b to e gives the distribution of oxygen, aluminum, titanium and yttrium within the particle and the surrounding alumina scale. It shows that the particle mainly contains titanium, yttrium and oxygen suggesting that mixed Ti/Y oxides form during oxidation. This type of oxide is thus likely to form both at the surface (Fig. 4) and within the scale.

The results presented above confirmed that the oxidation resistance of alloy PM2000 is excellent from 880 °C to 1230 °C. In this temperature range,

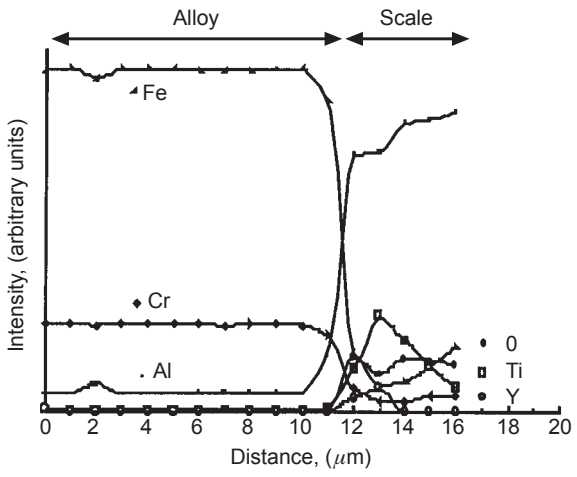


Figure 7 EPMA of the oxide scale and underlying matrix for specimen oxidized 240 h at 880 °C.

the exposure of the material to air provokes the formation of a slowly growing and adherent alumina scale. The good adherence of the scale is deduced from the absence of significant scale spallation even though specimens were cooled to room temperature before examination and analysis. For higher temperature, i.e., 1400 °C, the alumina scale formed during oxidation may crack and spall on cooling to room temperature in agreement with results reported in [5]. This decohesion is due to the differential strain arising from the difference in the thermal expansion coefficients of the matrix and scale. The propensity for scale decohesion to occur would be likely enhanced by thermal cycling. In this case, the critical temperature for oxide failure may be lower.

The continuous scale growth providing protective attack is mainly controlled by the inward diffusion of oxidant via oxide grain boundaries. The presence of Ti/Y rich nodules on the top of the oxide scales suggests that concurrent cation transport occurs throughout the oxide scale. However, as indicated in Fig. 3, this outward growth, promoting the formation of such nodules, occurs only locally and not on the whole scale surface, showing that the cation transport is quite limited. The tendency for titanium and yttrium to form mixed oxides can be related to the high thermodynamic stability of such oxides. This would account for the presence of Ti/Y rich particles not only on the scale surface but also within the growing scales. These compounds, mainly formed at oxide grain boundaries, can block the cation diffusion paths which hampers cation diffusion accross the scale. This was recently proposed as the role played by yttrium-rich compounds, to explain the change in growth mechanisms between yttrium or yttria free alloys and the corresponding ODS alloys [6]. As a consequence, the optimum oxidation resistance would be directly related to the amount and distribution of yttrium in the oxide scale.

The present experiments show that the growth rate of the oxide scale at 880 °C is much higher than expected. Although most results available in the literature show parabolic oxidation at temperatures 800–1000 °C, a deviation of the parabolic rate constant from an Arrhenius-type relation is often reported both in ODS FeCrAl alloys and in NiAl. The high values of the parabolic rate constants in NiAl for oxidation temperatures lower than 1000 °C was attributed to the occurence of a metastable θ-alumina [7]. In ODS FeCrAl alloys, literature reports two hypotheses to explain this deviation. The first [8], is that the amount of yttrium is not sufficient at 900 °C to effectively cause the optimum cation blocking. The second [8, 9] is related to the formation of metastable alumina similar to the phase formed on NiAl and observed in similar ODS alloy MA956 [10]. XRD experiments presented in this paper, correlated with SEM analysis, show that this phase did form on alloy PM2000 at 880 °C. It is concluded that the change in growth mechanism of the oxide scale is due to the change of structure of the growing alumina.

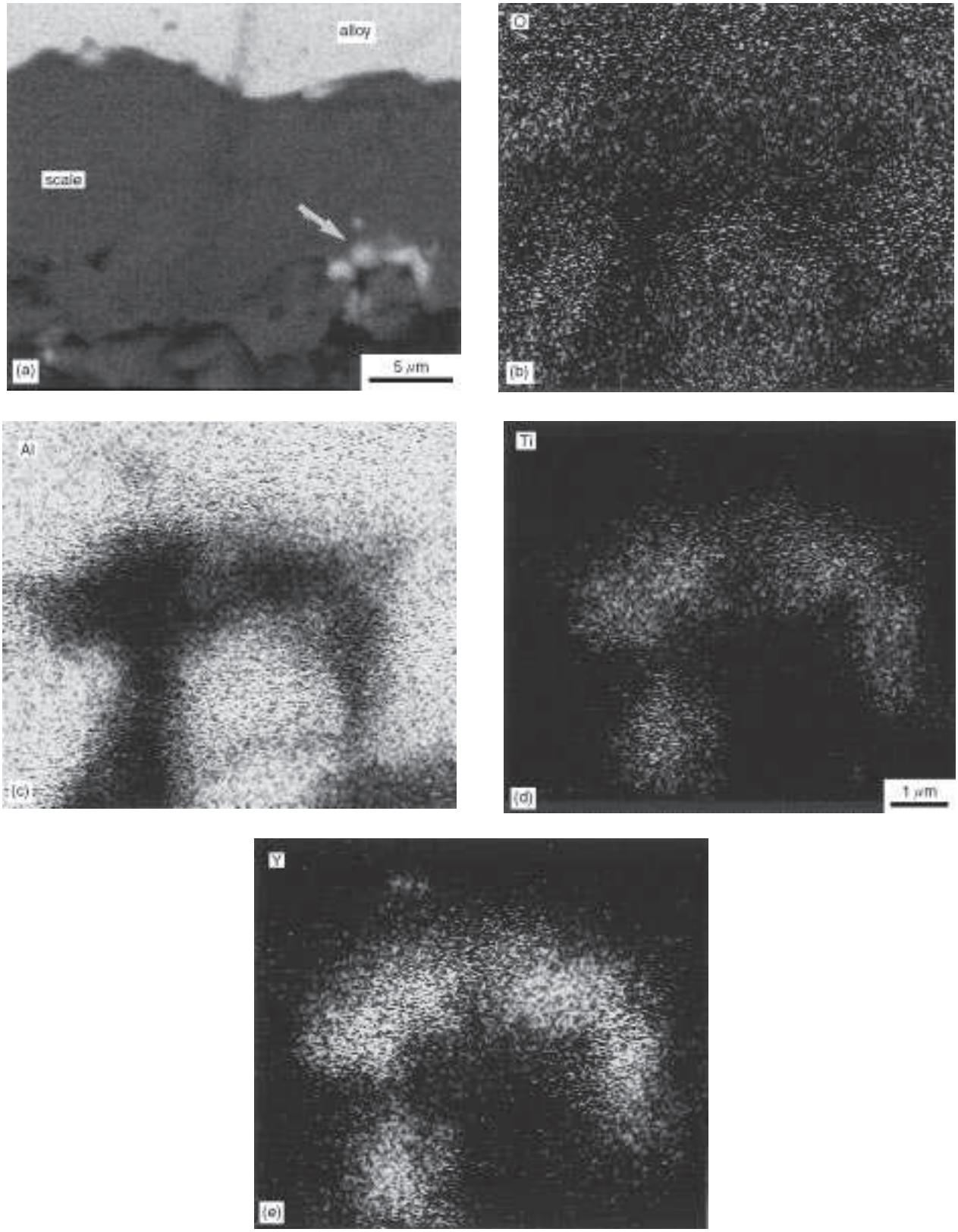


Figure 8 EPMA of the oxide scale for specimen after 100 h isothermal oxidation at 1400 °C, (a) corresponding SEM micrograph, (b) oxygen X-ray image, (c) Al X-ray image, (d) titanium X-ray image, (e) yttrium X-ray image.

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