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Accelerated oxidation of aluminides at intermediate temperatures

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Abstract. — The aluminides NbAl₃ and NiAl may show accelerated oxidation in a range of intermediate temperatures 600-1000 °C, especially at reduced oxygen pressures. Such pressures in the range 10⁻² to 10⁻³⁰ bar O₂ have been established for exposures in ampoules with the specimens, by enclosing also buffer mixtures such as Cu-Cu₂O, Fe₃O₄-Fe₂O₃, Ni-NiO etc. NbAl₃ disintegrates into small particles (pestring) and NiAl shows internal oxidation, general or localized, and oxidation along grain boundaries. Auger analyses after oxidation confirmed that oxygen penetrates into grain boundaries of NbAl₃ and NiAl. The transport of oxygen through the outer oxide layer appears to be rate controlling, in the case of NbAl₃ such transport is possible through Nb₂O₅ in the scale and in the case of NiAl through other defects caused by insufficient supply of oxygen in the exposures.

1. Introduction.

Many intermetallic phases have properties, such as low density, high melting point, and high strength at high temperatures which are very attractive for their use as high temperature materials. Several aluminides (NiAl, TiAl₃) and silicides (MoSi₂) form dense slow growing oxide scales, Al₂O₃ or SiO₂ resp., and show good oxidation resistance at high temperatures > 1000 °C. However, for some aluminides such as NbAl₃ [1, 2] and silicides such as MoSi₂ [3] a completely destructive oxidation may occur at intermediate temperatures which leads to disintegration into small particles. This phenomenon called "pest" was detected and studied about 30 years ago, but the authors could not completely elucidate the mechanism [4-10]. More progress is possible nowadays by the use of Auger electron spectroscopy (AES) to study the ingress of oxygen into the materials and the formation of very thin oxide layers at the intermediate temperatures [11]. Corresponding results are reported in this paper, on the pestring of NbAl₃, but also on the oxidation of NiAl under special conditions. Earlier works [12] lead to the conclusion that NiAl should form an external protective Al₂O₃ layer under any oxygen pressures and temperatures, however, in exposures of NiAl at temperatures between 700 – 1000 °C in ampoules with Cu-Cu₂O mixtures strong internal and external attack was observed. This oxidation behaviour of NiAl at reduced pressures was investigated in more detail using different equilibration mixtures and the results are also described in this paper.

2. Experimental.

For preparation of NbAl₃ at first a melt was produced in the vacuum induction furnace, after that the cast was milled and finally hot isostatically pressed at 1050 °C and 200 bar for 6 h. A dense homogeneous material was obtained, free of cracks and pores. Here, results are reported on the single phase material NbAl₃.

Four compositions within the stoichiometric range of β -NiAl were produced by vacuum induction melting, having the Ni/Al ratios: 60/40, 55/45, 50/50 and 45/55. The material with Al excess is very brittle and shows cracks. The materials with Ni excess were nearly free of cracks.

From these materials samples were cut by spark erosion. Oxidation experiments were conducted in He-O₂ mixtures but mostly in evacuated ampoules in the presence of different metal/oxide or oxide/oxide mixtures (see Tabs. I and II), which establish well defined low oxygen pressures in the range 10^{-2} ... 10^{-30} bar O₂. (The residual atmosphere in these ampoules, N₂, O₂, H₂O and hydrocarbons, equilibrates with the buffer mixture and was expected to warrant the oxygen transfer).

Table I. — Oxidation attack on NbAl₃ at 750 °C.

oxygen pressure range environment	observations	effect
0.1 to $5 \cdot 10^{-6}$ bar He-O ₂ gas mixtures	oxygen penetration into grain boundaries, Al ₂ O ₃ formation starting near the surface	stepwise dis- integration
$2 \cdot 10^{-10}$ to $7 \cdot 10^{-16}$ ampoules with Cu-Cu ₂ O- Ni-NiO	oxygen penetration into grain boundaries, uniform concentration throughout the specimen, abrupt Al ₂ O ₃ formation	abrupt dis- integration
$< 10^{-24}$ bar O ₂ NbO ₂ -Nb ₂ O ₅ Cr-Cr ₂ O ₃	oxygen penetration into grain boundaries, no Al ₂ O ₃ formation	no dis- integration

For AES analyses notched specimens were fractured by impact inside a UHV system, intergranular fracture faces were identified by the secondary electron image and analyzed by AES. The stoichiometric NiAl and samples with Al excess fracture intergranularly but often not at the notch, which indicates the presence of cracks; these can be distinguished from grain boundaries since they contain oxide particles even without oxidation or annealing. Both the Ni-rich materials fracture transgranularly at the notch before exposure; only after oxidation they show intergranular fracture. Thus, it may be concluded that these materials have no cracks and have oxygen-free grain boundaries as long as they fracture transgranularly, therefore only these materials have been used in the AES investigations.

Table II. — Oxidation attack on NiAl at 827 °C.

Oxygen pressure	equilibration mixture	attack	comment
$3.4 \cdot 10^{-2}$	BaO-BaO ₂	+	pocks
$2.5 \cdot 10^{-3}$	Cu ₂ O-CuO	+	general
$3.5 \cdot 10^{-9}$	Cu-Cu ₂ O	+	general
$3.5 \cdot 10^{-9}$	BaCO ₃ -BaO-Cu-Cu ₂ O	+	few small pocks
$1.4 \cdot 10^{-9}$	BaCO ₃ -BaO	-	
$2.1 \cdot 10^{-9}$	Fe ₃ O ₄ -Fe ₂ O ₃	+	many pocks
$6.3 \cdot 10^{-11}$	Pb-PbO	+	few pocks
$3.5 \cdot 10^{-14}$	Ni-NiO	+	many pocks
$1.9 \cdot 10^{-22}$	NbO ₂ -Nb ₂ O ₅	+	few small pocks
$2.8 \cdot 10^{-28}$	Cr-Cr ₂ O ₃	-	

3. Results.

3.1 PESTING OF NbAl₃. — The “pestring” of NbAl₃ is a complete disintegration of the material in a fine powder of oxidized particles (see Fig. 1). Pesting of NbAl₃ occurs at intermediate temperatures between 600-1000 °C; the maximum rates are observed at 750 °C and reduced pressures between about 10^{-20} and 0.1 bar O₂ [1, 2]. AES analysis of samples fractured inside of the UHV system after oxidation at 750 °C shows penetration of oxygen into the grain boundaries of the material. The spectra in figure 2 demonstrate the state of the intergranular fracture facets analyzed; a) in the center of the sample without oxygen; b) covered with oxygen which had penetrated into the grain boundary; c) with oxygen and Al₂O₃; and d) near the surface covered with Al₂O₃. This sequence indicates that oxygen can diffuse into grain boundaries of NbAl₃ and with increasing oxygen concentration, Al₂O₃ is formed in the grain boundaries, its growth eventually leading to spontaneous fracture of the material. In this process additional defects, e.g. dislocations may be generated into which oxygen can penetrate, otherwise the disintegration to very fine particles is not understandable.

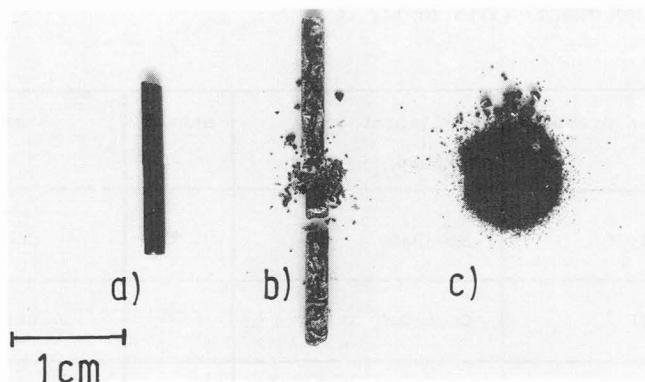


Fig. 1. — Pesting of NbAl_3 at 750°C and 2×10^{-10} bar O_2 : a) after 10 min; b) after 1 h; c) after 24 h oxidation.

In contrast to temperatures above 1000°C , NbAl_3 is not selectively oxidized to Al_2O_3 at the lower temperatures, since after short time oxidation Al_2O_3 and Nb_2O_5 were observed. Obviously, the presence of Nb_2O_5 allows access of oxygen through the oxide layer to the grain boundaries in the metal phase. The rate of pesting is highest at oxygen pressures between about $10^{-10} - 10^{-15}$ bar O_2 . The AES analyses show that under these conditions the oxygen penetrates through the whole cross section of the sample and later abrupt oxide formation follows when the oxide solubility product is exceeded; this leads to abrupt disintegration. Obviously, the supply of oxygen from the gas atmosphere through the outer oxide layer is rate determining for the oxygen ingress at these pressures. At higher oxygen pressures the oxygen supply is higher, an oxygen concentration gradient builds up in the grain boundaries and leads to Al_2O_3 formation in the outer region, retarding the oxygen ingress. At very low pressures $< 10^{-20}$ bar O_2 , the oxygen supply is too slow and within long-term exposures of 500 h no pesting was observed. Accordingly, the pesting of NbAl_3 comprises the following steps: 1) penetration of oxygen through the thin oxide layer formed at intermediate temperatures, presumably through Nb_2O_5 ; 2) diffusion of oxygen in grain boundaries into the aluminide; 3) precipitation of Al_2O_3 at the grain boundaries; 4) generation of dislocations into which the process continues and 5) cracking of the material by the alumina growth.

3.2 NiAl - INTERNAL OXIDATION AND POCKS FORMATION. — In the same temperature range but in a more restricted range of pressures, accelerated oxidation of NiAl was observed, comprising different phenomena. At about 10^{-10} bar O_2 (as established by a Cu-Cu₂O mixture) the strongest attack occurs, internal oxidation along grain boundaries and general oxidation starting from the surface both under formation of Al_2O_3 (see Fig. 3a). At somewhat higher or lower oxygen pressures, the oxidation is mainly local, the samples look as if covered with pocks (Fig. 3b, c), formed by outward and inward growth of a double cone of reaction products. These phenomena occur for example at 827°C in a pressure range 10^{-3} to 10^{-22} bar O_2 , which could be established by different metal/oxide or oxide/oxide mixtures (see Tab. II).

The oxidation of NiAl at 700°C in the atmosphere established by a Cu-Cu₂O mixture in an ampoule always leads to general attack of the whole sample, and the kinetics of this oxidation process was studied in detail. Samples were exposed for different periods of time and their mass increases determined; in a double-logarithmic plot of Δm vs. t with the slope $m = 1$ is obtained, i.e. a linear time dependence of oxidation is observed (Fig. 4). The mass gain is much faster than in the oxidation at normal pressures, as can be seen from the mass gain at

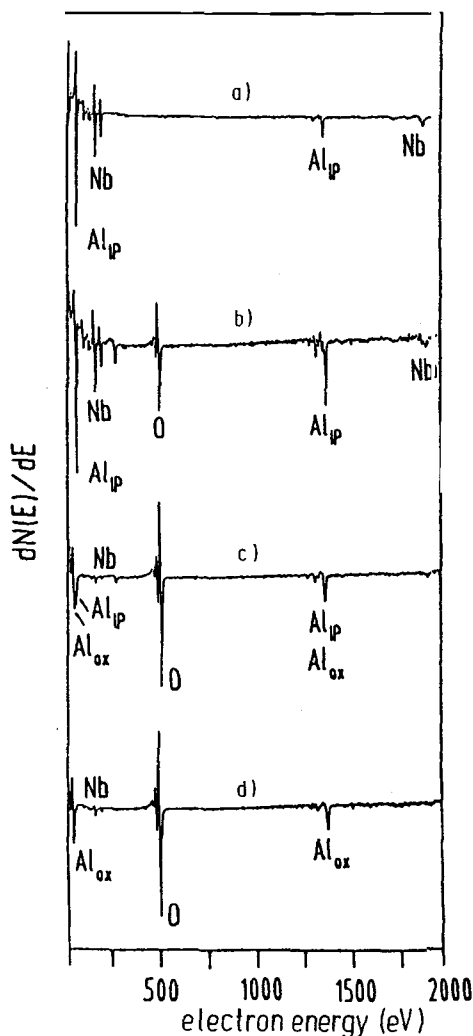


Fig. 2. — Auger spectra of the fracture surface of NbAl_3 after oxidation at 750°C : a)-d) different states with increasing oxygen ingress.

133 mbar O_2 at 700°C which is about two orders of magnitude lower and follows a parabolic rate law.

Oxygen ingress at grain boundaries of NiAl was demonstrated by AES analyses of samples annealed at about 10^{-10} bar O_2 (in equilibrium packs with $\text{Cu-Cu}_2\text{O}$). Figure 5 shows AES spectra of the fracture surface of NiAl after oxidation at 700°C and 10^{-11} bar O_2 : a) no oxygen, in the centre of the sample; b) covered with oxygen diffused into the grain boundary, but with no Al_2O_3 ; and c) near the surface, covered with Al_2O_3 . Accordingly, penetration of oxygen into grain boundaries is possible, also in NiAl as in NbAl_3 , maybe also diffusion into other defects such as dislocations.

Also the kinetics of oxygen ingress into the grain boundaries of NiAl was measured after exposures in the atmosphere established by $\text{Cu-Cu}_2\text{O}$ and proved to be linear. In figure 6 the percentage of grain boundary area covered by oxygen is plotted vs exposure time at 700°C

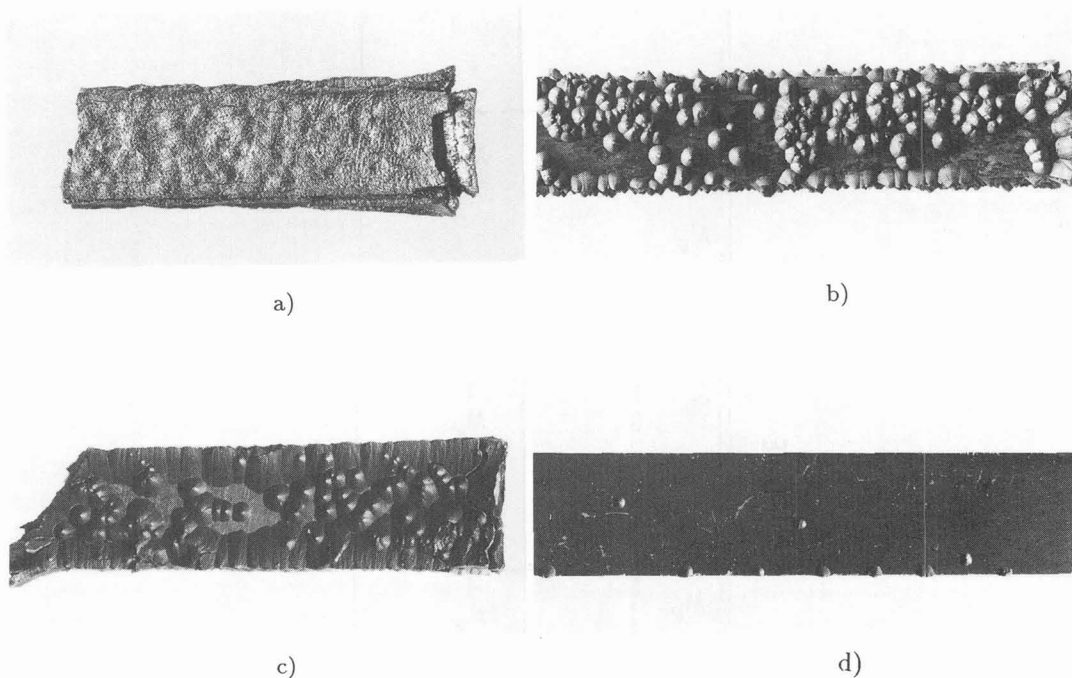


Fig. 3. — Photos of NiAl specimens after exposure at 827 °C in ampoules together with different buffer mixtures for establishing the $p(\text{O}_2)$: a) $\text{Ni}_{55}\text{Al}_{45}$ after 42 h with Cu-Cu₂O (6:1); b) $\text{Ni}_{55}\text{Al}_{45}$ after 48 h with Fe_3O_4 - Fe_2O_3 (6:1); c) $\text{Ni}_{50}\text{Al}_{50}$ after 43 h with Ni-NiO (8:1); d) $\text{Ni}_{55}\text{Al}_{45}$ after 96 h with BaCO_3 -BaO-Cu-Cu₂O (7:1).

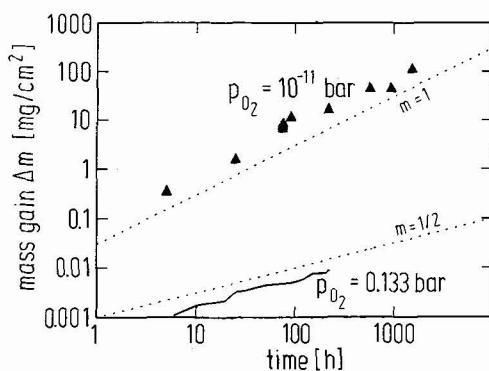


Fig. 4. — Mass gain of $\text{Ni}_{50}\text{Al}_{50}$ at 700 °C upon oxidation at 133 mbar O_2 and at 10^{-11} bar O_2 (in presence of Cu-Cu₂O).

and 800 °C, respectively. After very long exposures Al_2O_3 was also detected near the surface.

There was no concentration gradient of oxygen from the surface to the centre of the NiAl sample, - both observations, the linear time dependence and the lack of a concentration gradient of the penetrating oxygen indicate that a surface reaction is determining the rate of

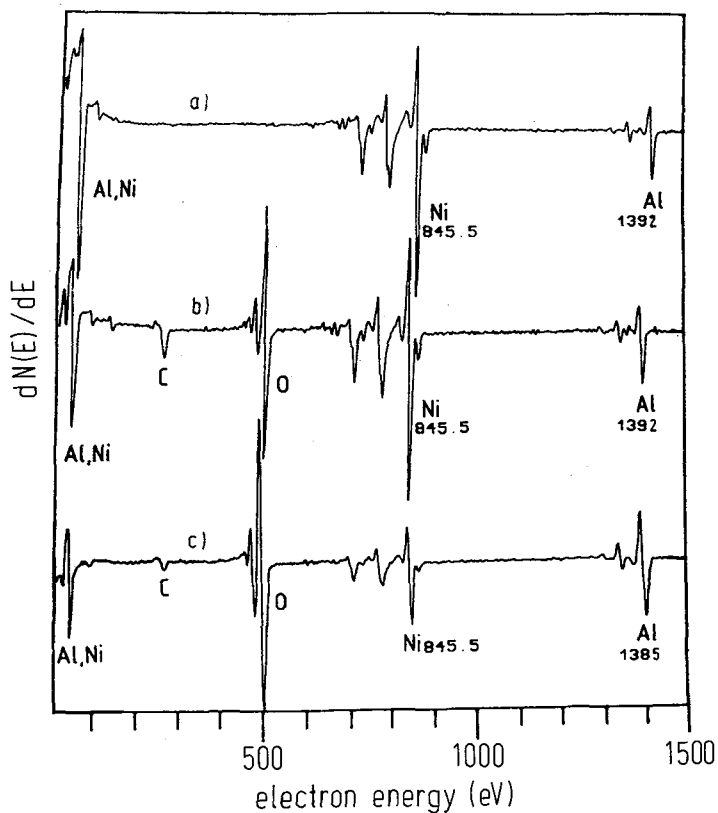


Fig. 5. — Auger spectra of intergranular fracture surfaces of NiAl after oxidation at 700 °C and 10^{-11} bar O_2 (in presence of Cu-Cu₂O); a)-c) in different states of oxygen ingress.

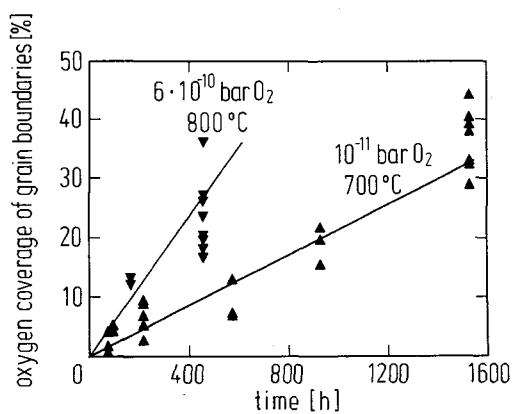


Fig. 6. — Oxygen coverages determined by AES on intergranular fracture faces of NiAl after exposures at 700 °C and 800 °C (in the presence of Cu-Cu₂O) for different times.

oxygen ingress into the material and also the oxidation rate. After short periods < 500 h, the oxidation attack is still non-uniform but after longer time a broad front of internal oxidation progresses into the interior (see Fig. 7), oxide formation at grain boundaries is preceding. A fringe of Al-depleted material can be seen, at the oxidized grain boundaries its composition corresponds to Ni-rich NiAl, in the internally oxidized region Al-rich Ni₃Al is formed. The behaviour of different stoichiometries is not different concerning the internal oxidation.

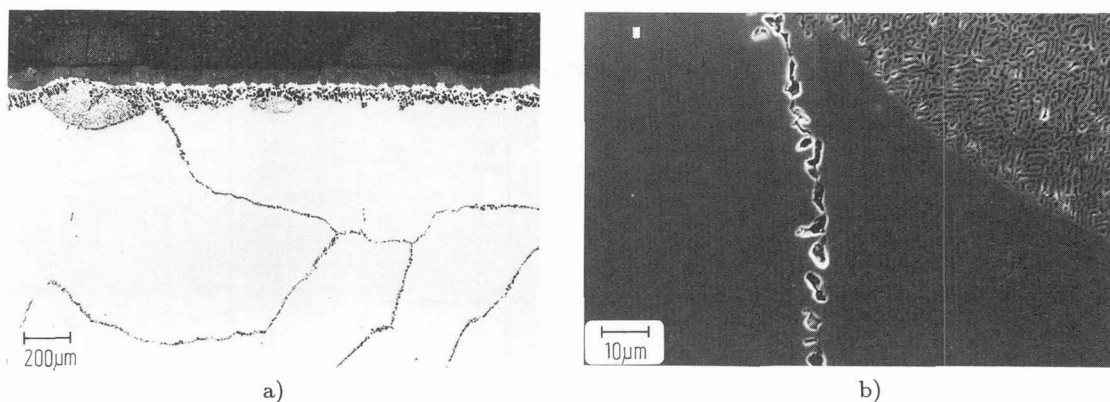


Fig. 7. — Metallographic cross sections of NiAl, internal oxidation and grain boundary oxidation: a) Optical micrograph after 454 h at 800 °C and 6×10^{-10} bar O₂ (Cu-Cu₂O); b) REM-photo after 1.153 h at 700 °C and 10^{-11} bar O₂ (the Al₂O₃ particles have fallen out from the grain boundary).

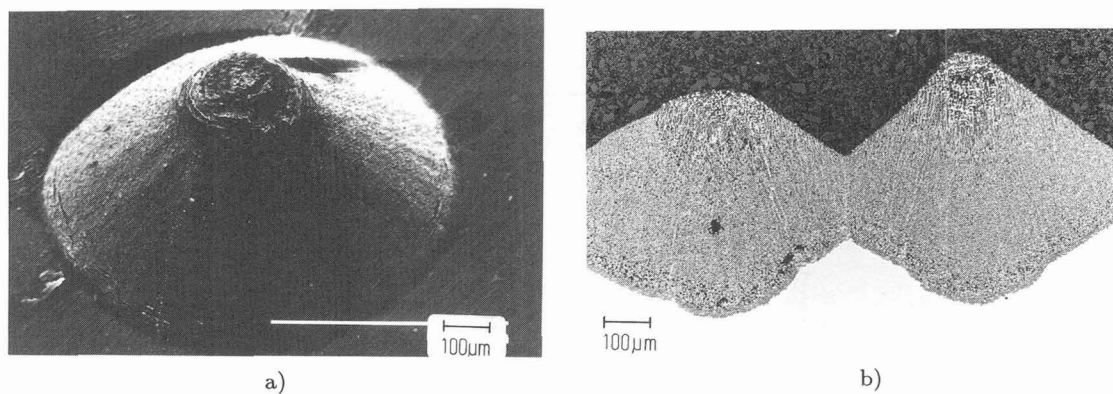


Fig. 8. — Local attack of NiAl at 827 °C and 2×10^{-9} bar O₂ (Fe₃O₄-Fe₂O₃): a) SEM photo of an overgrown cone; b) metallographic cross section after 48 h.

Both phenomena, general and localized attack of NiAl, are suppressed at higher oxygen pressures, obviously by formation of a protective oxide scale. The question arose whether the corrosion phenomena were not only caused by the low oxygen pressure in presence of

buffer mixtures, but mainly by insufficient oxygen supply. A faster oxygen supply from the gas phase could be achieved by establishing an H_2 - H_2O or CO - CO_2 atmosphere at the oxygen pressure given by the buffer mixture Cu - Cu_2O . This was possible by using mixtures such as Cu - Cu_2O - $Ba(OH)_2$ - BaO or Cu - Cu_2O - $BaCO_3$ - BaO . The resulting H_2O - H_2 or CO_2 - CO atmospheres should warrant a well-defined low oxygen pressure but a faster oxygen transfer, avoiding oxygen depletion in the formation of the protective Al_2O_3 scale on $NiAl$. Indeed, ampoule experiments in which the atmosphere was generated by such mixtures lead to less attack, the internal oxidation and pocks formation was largely suppressed (see Fig. 3d). Furthermore, oxidation experiments in flowing CO_2 - CO mixtures but low oxygen pressures did not lead to internal oxidation of $NiAl$ but to formation of a thin protective scale.

The result indicates that low oxygen pressure is necessary for occurrence of the oxidation phenomena described but most probably also insufficient oxygen supply in the start of the experiments so that no protective alumina was formed. The oxide layer formed in the ampoule experiments with buffer mixtures is permeable for oxygen and the supply of oxygen from the gas atmosphere to the intermetallic phase controls the rate of its oxidation. Oxygen can penetrate into grain boundaries of $NiAl$ but most probably also into other defects such as dislocations, this leads to a localized or general attack. As yet it is not clear why some conditions cause localized attack and pocks formation and the exposure with Cu - Cu_2O a general attack.

Acknowledgements.

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References

- [1] STEINHORST M., GRABKE H.J., *Mater. Sci. Eng.* **A 120** (1989) 55.
- [2] STEINHORST M., GRABKE H.J., *Z. Metallkd.* **81** (1990) 732.
- [3] BERKOWITZ-MATTUCK J.B., BLACKBURN P.E., FELTEN E.J., *Trans. Metall. Soc. AIME* **233** (1965) 1093.
- [4] AITKEN E.A., *Intermetallic Compounds*, J.H. Westbrook Ed. (J. Wiley, New York, 1967).
- [5] WESTBROOK J.H., WOOD D.J., *J. Nucl. Mater.* **12** (2) (1984) 208.
- [6] GLEITER H., CHALMERS B., *Prog. Mater. Sci.* **16** (3) (1976) 43.
- [7] HAGEL W.C., WESTBROOK J.H., *Trans. AIME* **221** (1961) 600.
- [8] SEYBOLT A.U., WESTBROOK J.H., *Acta Metall.* **12** (1964) 449.
- [9] DARKEN L.S., *Trans. Am. Soc. Metall.* **54** (1961) 600.
- [10] TURNER P.A., PASCOE M.T., NEWLEY C.W.A., *J. Mater. Sci.* **1** (1966) 113; *J. Mater. Sci.* **2** (1967) 197.
- [11] GRABKE H.J., BRUMM M., STEINHORST M., *Fresenius Z. Anal. Chem.* **341** (1991) 378.
- [12] PETTIT F.S., *Trans. AIME* **239** (1967) 1296.