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Oxidation of advanced intermetallic compounds

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Abstract. — Intermetallic compounds with low densities and high melting temperatures are prime structural material candidates for advanced heat engines. The close link between crystal structure and mechanical properties has led the search for new cubic pseudo-binary transition metal aluminides. Compositing leads the way for improved mechanical properties of refractory metal silicides. In all cases there is a strong competition for oxide scale frequency between the energetic oxide formers of the intermetallic compounds. In the case of titanium aluminides, efforts are directed towards modification of the concentration of oxygen vacancies to reduce growth rates and influence scale dominance. Glass formers are added to the disilicides to promote scale fluidity to seal cracks which are pathways for oxidation.

1. Introduction.

The most successful intermetallics are coatings. The most successful coatings are the intermetallics based upon the aluminides of the transition metals notably nickel, cobalt and iron. The remarkable growth of the gas turbine superalloys is based in part upon the ability of the material engineer to concentrate efforts to improve mechanical properties and employ coatings to achieve acceptable oxidation and corrosion resistance.

Further increases in efficiency and performance of gas turbine engines is possible through the use of materials that can operate at higher temperatures and possess greater strength to weight ratios. Intermetallic compounds are candidate materials. The nickel aluminides are more refractory than the current transition element alloys. The aluminides of titanium promise higher strengths with lower densities, while composites based upon molybdenum disilicide offer high temperature strength and oxidation resistance. Thus the objective of this address is to identify current strengths and weaknesses in order to further promote the state-of-the-art.

2. Oxidation resistance.

Oxidation resistance is often the limiting factor that determines the life of high temperature structural metals and alloys. The kinetics, morphology and composition of the oxidation products are obtained from thermogravimetric analytical studies (TGA), light and electron microscopy studies, and various analytical techniques. All of the above are used to determine the rate of growth of the oxidation products. The rate of growth of the oxidation products are often described by a parabolic function and the relative merit of performance is commonly presented in pictorial form as a plot of the log of the parabolic scaling constant *versus* the reciprocal of the absolute temperature.

Although the rate of growth of the oxide scale, determined from isothermal studies is a measure of performance; it is, at best, a poor yardstick. Oxidation resistance is not only a measure of the rate at which an oxide scale thickens, but includes the ability of the scale to resist the thermally induced stresses associated with cyclic behavior. A typical example is the relative behavior of the materials, Ni-15Cr-6Al and Ni-15 Cr-6Al-0.1Y. In isothermal tests both materials form alumina scales. However in a cyclic test the yttrium-containing alloy maintains its ability to form a protective adherent oxide scale. However the alumina scale on the yttrium free alloy spalls at the completion of each cycle (Fig. 1). Thus although both alloys form alumina scales, the alloy containing yttrium exhibits "oxidation resistance". If intermetallic compounds are to be structural components operating in oxidizing environments, they must exhibit both the necessary mechanical properties as well as oxidation resistance. It is therefore important to understand the factors that influence oxide scale adherence.

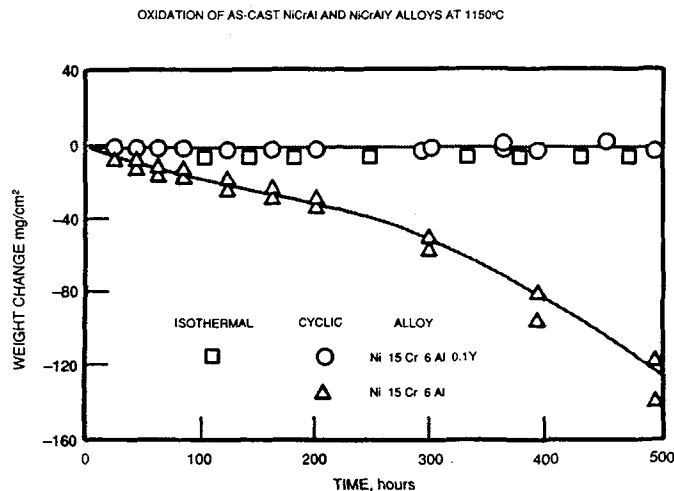


Fig. 1. — Yttrium greatly enhances oxide scale adherence.

3. Alumina formers.

3.1 NICKEL BASE ALLOYS. — Tien *et al.* [1] describing cyclic oxidation says "violence is done on oxide scales during cyclic oxidation by growth and thermal stresses". It is well established that the addition of small quantities of certain elements and compounds greatly improves oxide scale adherence. The phenomena is called the "reactive element effect" (REE). A number of mechanisms have been proposed and reviewed [2, 3]. Yttrium is the most commonly used reactive element to impart scale spallation resistance to alumina forming alloys. Recently it has been proposed that the alumina scale that forms on the transition metal alloys and compounds is strongly bonded, but impurities present in the substrate promote oxide scale spallation. The principal impurity is sulfur. It is important to establish if the removal of sulfur below some critical level imparts oxidation resistance since it is not always commercially feasible to add reactive elements without incurring other liabilities.

The sulfur model is the product of ONR-sponsored research to explain the improvement observed in oxide scale adherence when surfaces are laser processed [4]. The strength of the model is its simplicity. The model assumes the existence of a strong chemical bond between the alumina scale and the alloy substrate. The bond is weakened by sulfur, a tramp impurity, which segregates to the oxide scale interface. The mechanism by which sulfur weakens the bond is not described, however it is proposed that superior oxide scale adherence is achieved by reducing the activity of sulfur in the substrate either by removal of sulfur or uniting the sulfur with a potent sulfide former. The role of the REE is to unite with and thereby reduce the activity of sulfur in the substrate.

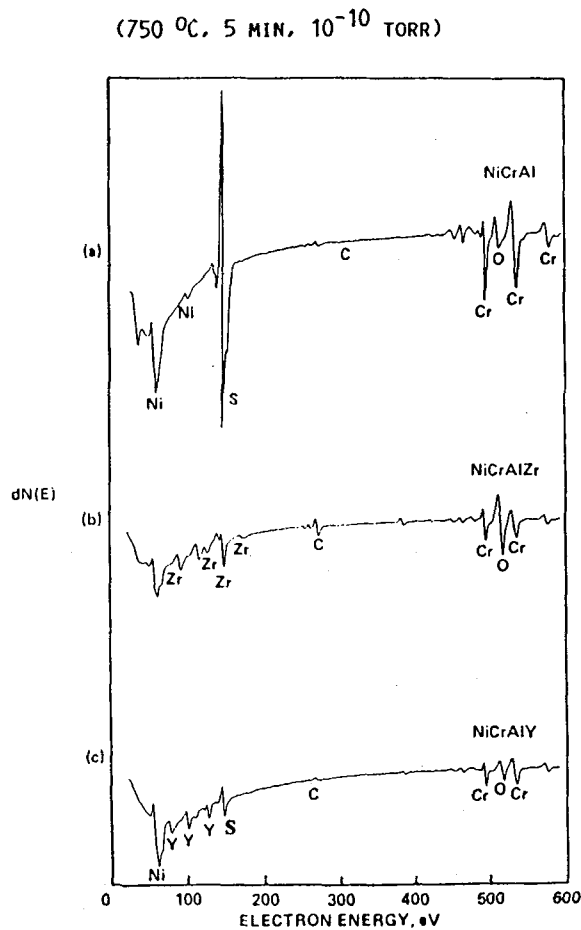


Fig. 2. — Auger spectra showing S, Zr or Y segregation.

Auger studies are used to demonstrate that the reactive elements reduce the activity of sulfur in Ni-Cr-Al alloys, figure 2 [5]. Other studies have shown that the addition of sulfur to NiCrAlY alloys results in the formation of sulfur-containing oxidation-resistant scales. However, the

addition of more yttrium restores resistance to oxide scale spallation (Fig. 3). This data supports the sulfur-yttrium interaction. However the recent work of Smialek *et al.* [6] strongly indicates that the simple reduction in the concentration of sulfur in the matrix is sufficient to impart resistance to oxide scale spallation. The heat treatment of nickel base alloys in hydrogen environments was used to remove sulfur from the alloy, and the subsequent high temperature cyclic oxidation tests verified the formation of a spallation resistant oxide scale.

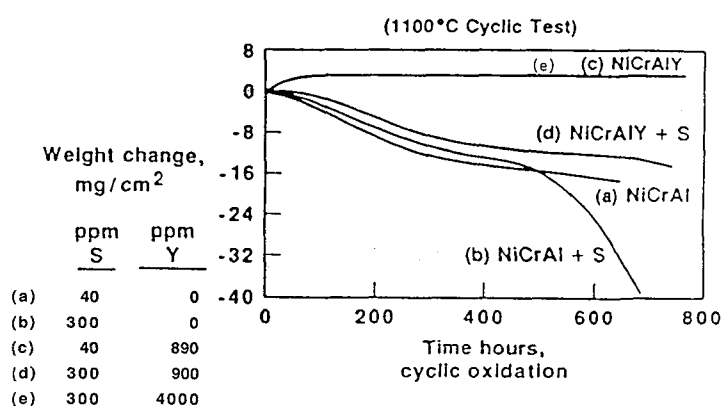


Fig. 3. — Effect of yttrium and sulfur content on the cyclic oxidation resistance of NiCrAl.

The intermetallic compound NiAl is quite brittle at low temperatures and rather weak at elevated temperatures. Nevertheless it is suggested for use in advanced applications as the matrix phase for metallic based composites. The face centered cubic intermetallic compound Ni₃Al, when alloyed with small quantities of boron, exhibits attractive mechanical properties over a wide range of temperatures. Although the oxidation behavior of NiAl has been extensively studied, further improvements, taking into account the role of sulfur, should be explored. The oxidation behavior of boron modified Ni₃Al with respect to sulfur and oxide scale adherence should be investigated.

3.2 TITANIUM ALUMINIDES. — Alloy designers are concerned with finding materials with superior properties. In the aircraft industry new light weight strong oxidation resistant materials are sought. Some of the most attractive aluminides from the view point of low density and high temperature potential are those in the Ti-Al system such as Ti₃Al and TiAl. Their densities of 3.76 to 4.50 g/cm³ are only half the densities of nickel and cobalt superalloys. Large weight savings are possible, however the use of titanium aluminides at high temperature is limited by relatively poor oxidation resistance.

Titanium and aluminium are both energetic oxide formers. It is generally agreed that alumina is the scale that forms on the surface of TiAl₃. However this very brittle intermetallic compound draws little interest.

Meier *et al.* [7] using the criteria established by Wagner [8] and data available in the literature conclude that the solubility of aluminum in titanium in both the alpha and beta phases is insufficient for the alloy to develop an alumina protective external scale. The aluminum

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