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Surface phenomena in a precipitation-hardenable nickel–chromium alloy during multiple heating/cooling

Stanislaw Adamiak [a], Nicolas Berchenko [b,*], Wojciech Bochnowski [a], Andrzej Dziedzic [a], Malgorzata Trzyna [b], Sergey Fadeyev [c], Josef Cebulski [a]

[a] Center of Innovation & Knowledge Transfer, Lab. 1, University of Rzeszow, Pigonia 1, 35-310 Rzeszow, Poland
[b] Center for Microelectronics and Nanotechnology, University of Rzeszow, Pigonia 1, 35-310 Rzeszow, Poland
[c] Lviv Polytechnic State University, Bandera St., 12, Lviv 79646, Ukraine

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ABSTRACT

Time-of-flight secondary ion mass spectrometry profiling, scanning transmission electron microscopy, and energy dispersive X-ray mapping were used to investigate physical and chemical processes on the surface of a precipitation-hardenable nickel–chromium alloy associated with single or multiple heating/cooling cycles that simulate typical service conditions of aircraft products made of such alloys. Research findings show the growth of oxide, increase of surface roughness, and microstructural changes. The depth distribution of main metal oxides is discussed. It was determined that aluminum diffusing along the alloy grain boundaries forms an oxide on the surface and intergranular Al_2O_3. The Ti and Nb nitride inclusions were found to appear after the first oxidation cycle.

1. Introduction

Inconel, a family of nickel–chromium based superalloys, is widely used in many industries, in the aircraft industry. Most elements made of Inconel work under high mechanical stress with periodic changes of temperature up to 700 °C. Identification of physical and chemical processes occurring on the surface of this material is of great importance for its further use and application in new industries [1–3]. To obtain the predetermined properties many elements were included in the Inconel X-750 alloy composition. This makes it, in comparison with the other well studied ternary Ni–Cr–Fe-based superalloys, also an interesting object of study on the interaction during the oxidation in multi-component metallic systems. The objective of this work is chemical characterization of a composition of oxide films grown on Inconel X-750 samples subjected to cyclic thermal treating.

2. Experimental details

Commercially available samples of Inconel X-750 (Special Metals Co.) with nominal chemical composition in wt.% — 70 Ni, 14–17 Cr, 5–9 Fe, 2.55 Ti, 0.77 Al, 0,94 (Nb + Ta) with Mn, Si, Cu, C and S as minority alloying elements were used in experimental studies. The composition of initial samples and standard aged ones was determined before oxidizing. The formation of a surface layer under cyclic oxidation was particularly thoroughly studied.

Saturated X-750 superalloy samples (according to standards) were heated to 700 °C followed by cooling in an oven. Heating and cooling took place in the ambient air. The samples were explored under the next modes: a) a single heating/cooling cycle; b) ten heating/cooling cycles. The heating rate was 100 °C/min; the samples remained at 700 °C for 1 h; the cooling rate was about 50 °C/min.

The samples to be studied under a transmission electron microscope (TEM) were cut out using a FEI Quanta 3Di electron-ion microscope (Fig. 1a). The TEM (FEI Tecnai Osiris) allows for the imaging of the surface topography of a sample, comprising energy dispersive X-ray (EDX) spectroscopic chemical analysis. The focused ion beam (FIB) technique allows cutting out various shapes from a sample, including lamellas suitable for analysis based on different TEM techniques. To obtain a good image contrast, Z-contrast imaging generated by high angle

* Corresponding author. Tel.: +48 17 8518663; fax: +48 17 851 8516.
E-mail addresses: nberchen@gmail.com, nberchen@ur.edu.pl (N. Berchenko).

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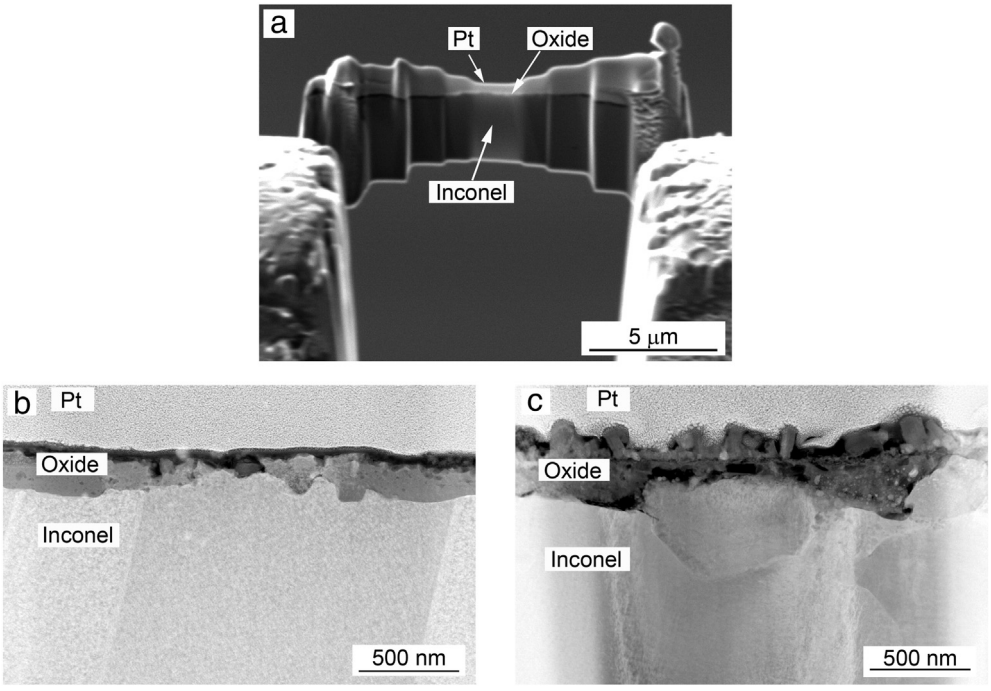

Fig. 1. Lamella ready for measurement (a) and STEM-HAADF images of Inconel X-750 alloy after a single (b) and tenth (c) heating and cooling cycles.

annular dark field (HAADF) scanning transmission electron microscopy (STEM) was used.

Atomic Force Microscope (AFM) imaging in non-contact mode was performed in air, at room temperature using the AFM from CSM Instruments. Time-of-flight secondary ion mass spectrometry (TOF-SIMS) data were acquired using a TOF-SIMS V spectrometer (ION-TOF GmbH, Muenster, Germany). The analysis chamber was maintained at less than 5×10^{-10} Pa under operational conditions. A pulsed 30 keV Bi^+ primary ion source at a current of 1.3 pA (high current bunched mode), rastered over a scan area of 50 × 50 μm while keeping the fluence of 4.87×10^{13} ions/cm^2 was used as the analysis beam. TOF-SIMS depth profiles were measured with the instrument working in the dual-beam mode. The sputtering was performed using a 2 keV (80 nA) Cs^+ ion beam, rastered over an area of 150 × 150 μm. Both ion beams were impinging the sample surface forming a 45° angle with the surface normal and were aligned in such a way that the analyzed ions were taken from the center of the sputtered crater. Data acquisition and processing analyses were performed using the commercial SurfaceLab program.

3. Results and discussion

The evaluation of the effect of multiple processing cycles was conducted by comparing STEM-HAADF images Fig. 1b, c obtained for samples after a single heating/cooling cycle and ten heating/cooling cycles. This comparison shows an increased oxide thickness. The thickness of oxide layer on the cross-section is in the range of 25–130 nm after a single heating/cooling cycle, and it is in the range of 100–550 nm after ten heating/cooling cycles. There is also the change of the microstructure, including the dimension and shape of grains. The latter, in turn, increases the surface roughness that is confirmed by the surface topography. In accordance with the atomic force microscopy, the mean value of surface roughness R_A is 8.1 nm for the initial sample, and it increases to 12.3 nm after a single cycle and 19.1 nm after 10 cycles.

The post-thermal-aging change of the chemical composition of surface oxides was studied using TOF-SIMS profiling and EDX mapping. Fig. 2 presents a typical TOF-SIMS negative ion depth profile of the sample after ten heating/cooling cycles. In Fig. 2a, the counts associated with oxygen and simplest main oxides ions (NiO^- and the like) are plotted versus Cs^+ ion sputtering time. In Fig. 2b the profiles of the minor elements oxides (NbO^- and the like) are presented; here the intensity is shown using the logarithmic scale, which emphasizes the low intensity signals.

The elements in the oxide are redistributed as compared to the starting material that is characteristic of Cr–Fe–Ni alloys [3]. The outer oxide part would be composed of a mixed Ni and Fe rich layer, the intermediate layer would be Cr, oxides-rich. The distribution of Ti and Nb oxides which are not in Inconel Alloy 690 [3] should be discussed separately. The NbO maximum is seen to be located at the interface of Ni/Fe and Cr rich layers, while the TiO maximum, on the other hand, is closer to the interface with the alloy. This is also a position of the layer mainly characterized by the NiCrO which would correspond to a spinel-rich $NiCr_2O_4$ [3]. The pattern of how oxides are distributed throughout the alloy is formed mainly during the first thermal cycle and remains largely unchanged after ten cycles in a first approximation. The principal features of element distribution are shaped in early phases of oxidation. It occurs due to the preferential oxidation of some metals because of energetic benefits of some oxidation reactions. We have estimated all ternary diagrams of Cr, Fe, Ni and Ti with oxygen using the phase equilibrium diagram method [4]. All the diagrams show that oxidation begins with oxidizing one of the metals as shown for Fe–Ni–O and Fe–Cr–O (Fig. 3). In Fe–Cr–O system, oxidation begins with Cr_2O_3 formation, but for Fe–Ni–O the picture of oxidation is qualitatively different, as Fe oxides are formed first. In multicomponent alloys and Inconel X-750 in particular, these reactions compete according to the energy benefit they provide. Formation of ternary oxides makes the phenomenon even more complicated.

Since almost all metals in the alloy have a few stable oxides, we must determine molecular chemical signatures [5,6] to ensure reliable identification of these oxides. We attempted to carry out this

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