Investigation the Al–Fe–Cr–Ti nano composites structures with using XRD and AFM techniques

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Abstract. The performance of multilayers has been widely investigated in metal/metal systems. Shrinking this system down to less than 10 nm dislocation blocking occurs. We should thus try to find a way to get a structure with less dislocation, and/or strain because low diffusivity ultra high vacuum chamber is the basic requirements for growing ultra thin films and nano scale materials. We used William–Hall relation based on Scherr equation in X-ray powder spectrum and drawn the stress–strain diagrams. It shows that Al–Fe–Cr–Ti composites have very low diffusivity and equilibrium solubility in Al (0.05 at.% Fe, >0.02 at.% Cr, and >0.3 at.% Ti). Al–Ti–Fe–Cr composite powders have also been prepared from sol–gel method starting from elemental powders at both ambient and elevated temperatures. The obtained results from XRD (X-ray Diffraction), AFM (Atomic Force Microscopy) and X-ray powder techniques indicate that nano-grains with 0.03 at.% Cr can cause a reduction of leakage current through the SS chamber due to its amorphous structure.

Keywords. Nano composite; aluminum; sol–gel method and XRD; AFM techniques.

1. Introduction

Some researchers (Yang *et al* 1992; Morgen *et al* 2005, 2007; Kalita *et al* 2008a; Bahari & Gholipur 2012; Pandey *et al* 2008; Inoue & Kimura 2000) have studied the nano scale multilayer coatings due to their high potential for numerous engineering applications. The metallic nano composites can exhibit enhanced properties due to nano scale effects and combine different

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properties from individual components. Indeed, bulk amorphous composites coupled with good bending ductility possess high tensile strengths (Yang *et al* 1992; Morgen *et al* 2007; Kalita *et al* 2008a). The more stable mechanical structure can be synthesized with amorphous phases (Hayes *et al* 2001; Bahari *et al* 2005; Belyakov *et al* 2001). The use of these structures can help chamber designers to control the residual strain and therefore the tensile stress within coatings, most commonly to enhance the effective adhesion and strength (Bahari *et al* 2005; Belyakov *et al* 2001; Zawrah & Shaw 2003). A nanoscale mixture of quasicrystalline phases surrounded by a continuous fcc-Al phase can affect on the tensile strength with changing the morphology and transformation phases of SS, AFM images and XRD patterns. We have demonstrated a series of experiments to synthesize Al–Ti–Cr–Fe composites via sol–gel method. The obtained results indicate that at the present gelling condition Cr atoms do not diffuse very far. It also explains why it is hard to find an Al grain with Cr solutes unless there is a Cr-rich particle around. In contrast, the Fe element can be found in most of the thin foil area even though there are no Fe-rich particles around. The chance to find an Al grain with Ti solutes is intermediate (Shaw *et al* 2003; Bahari *et al* 2006; Sun *et al* 2000; Yongxiang *et al* 2004).

Therefore, in designing ultra high vacuum chamber, we combined Al, Ti, Cr and Fe materials with different strength, toughness in the chamber structure, and adjust the grain size, the shape of the grains, the amount and constitution of individual crystallites. The AFM images and XRD patterns show grain boundary relaxation which can remove the voids in the chamber structure and reduce the leakage and tunnelling currents.

2. Experimental details

The sol–gel process is commonly applied to synthesis of such SS composite owing to its several advantages such as low temperature processing and the ability to prepare materials in various shapes, compared with the conventional preparation procedures of glass and ceramics (Shaw *et al* 2003; Kalita *et al* 2008b, 2009; Bahari *et al* 2006; Zhou *et al* 2006). In this work, we have prepared nano composite by using hydrolysis procedure of TiCl_4 , Al_2O_3 , Fe_2O_3 (JCPDS 33-664) and FeCr_2O_4 , which is transformed to the other crystalline phases by heating it at 300 to 900°C. It obviously depends on the preparation procedures and Ti, Al contents in combination.

In order to synthesize the SS gel, we used tetraethyl-orthosilicate (TEOS) (Merk, ≥ 99) which hydrolysed with di-ionized water and ethanol. The acetic acid was added to the solvent at room temperature for 30 min. The solution was then mixed with titanium chloride TiCl_4 , Al_2O_3 , Fe_2O_3 (JCPDS 33-664) and FeCr_2O_4 (Merk, ≥ 99) at 0°C in specific molar ratio to obtain various content of SS. After 30 min stirring at room temperature, the sol was vibrated for 20 more minute in ultrasonic bath to deconglomerate particles and then relaxed at room temperature for 30 min. The sol was stirred at 60°C until it became gel and removed ethanol (about 24 h). After gelation, samples were dried at 60°C to remove water and acetic acid and leave a white to light yellow lump depend on TiO_2 content. After that the lump samples were milled with mortar and calcinated in 300 and 900°C. The thermal gradient during experimental procedure was 5 deg/min and the samples were put in oven for 2 h at different calcination temperatures.

The composition, structure and surface morphology of the Al_2O_3 – TiO_2 – SiO_2 powder were investigated by using XRD, AFM techniques and the spectra and microscope's images are shown in figures 1, 2, 3 and 4.

Powders were analysed using XRD methods with CuK_α radiation. The XRD patterns were measured on X-ray powder diffractometer (GBC-MMA007 Australia) by using $K_\alpha(\text{Cu})$, 1.54 Å radiation, 0.05 step size where in the speed was 10 deg/min.

Figure 1. XRD patterns of Al-Fe-Ti-Cr composites gelled at different temperatures.

Figure 2. XRD patterns of Al-Fe-Ti-Cr composites gelled at 500°C and for different times, (a) 30 min, (b) 50 min, (c) 90 min and (d) 120 min.

Figure 3. 2D AFM image of Al-Fe-Cr-Ti nanoparticles in SS content. Magnification: X 1000.

Figure 4. 3D AFM image of Al-Fe-Cr-Ti nanoparticles in SS content. Magnification: X 1000.

In addition to monitoring the evolution of the crystal structure, X-ray powder was used to measure the crystallite size and internal strains (figures 5, 6, 7 and 8). Particle morphology and the distribution of elements within the particle were examined using a Nanosurf technique (figure 9).

It can be seen in XRD patterns and AFM images that Al, Fe, Cr and Ti peaks are hardly ascertainable even for the powder mixture because of their low concentrations and partial overlapping of their peaks with Al peaks. Thus, the detection of the formation of Al-Fe-Cr-Ti composites could only rely on the measurement of changes in Al reflections.

The peak position of Al reflections shifts to higher 2θ angles as the gelling time increases (figure 2), suggesting the formation of Al-based solid solutions and an increase in the solute concentration as the gelling time increases. All aluminum reflections exhibit broadening even after only 10 h of gelling, indicating the grain size reduction and possibly the introduction of internal strains, as found with X-ray powder patterns, in figures 3–6.

Figure 5. The size of nanoparticles correspond with figure 2, is 42 nm as determined with using X-ray powder method.

Figure 6. The size of nanoparticles correspond with figure 2 is 53 nm as determined by using X-ray powder method.

Figure 7. The size of nano-particle is 14.3 nm as determined by using X-ray Powder method.

Figure 8. The size of nano-particle is 31 nm as determined by using X-ray Powder method.

Figure 9. The size of nano-particle is 39 nm as determined by NanoSurf method.

Based on the broadening of the XRD peaks, the size of retained element crystallites was calculated. As shown in X-ray powder measurements, patterns in figures 5 through 8, it can be seen that the crystallite size of fcc-Al decreases rapidly at the early stage of process and gradually after prolonged synthesizing. The reason could be attributed to the internal strain computed from peak broadening is also included in figure 2. As expected, the internal strain increases in general with gelling times, suggesting the introduction of substantial amounts of defects in fcc-Al during synthesizing.

AFM images in figures 2, 4 and 9 revealed that there is a nanostructural gradient in the element particle. Individual Fe, Cr and Ti particles embedded in the Al matrix can be easily found near and at the central region of the AFM images as shown in Nnaosurf image in figure 9. However, the surface region contains no visible individual Fe, Cr and Ti particles, suggesting that Fe, Cr and Ti particles have been broken down to a very fine scale, or dissolved in the Al matrix to form solid solutions. They also reveal that the remaining Fe, Cr and Ti particles at the location of middle of AFM images in 3 dimensions (3D) away from the particle surface are either flattened or equalled. The size of the equalled particles is about 39 nm, as found with using *Nanosurf* method in figure 9, which is finer than that of the original Fe, Cr and Ti particles. These results suggest that flattening and breaking down of the coarse compositing particles into fine equalled particles precede the dissolution process of these compositing elements into the fcc-Al matrix.

It seems impossible to label Fe, Ti, Cr and Fe in AFM images, but in the present cases (see topography spectrum in figure 10), the edge crack corresponding to the crack plane parallel to that of the interface between Al/Fe and Al/Ti boundaries. The darker area is due to the plastic deformation of the tough layers that bridge the crack behind the position of the crack tip in the brittle layers.

The stress–strain diagram of the samples are measured with Nanosurf technique and Williamson–Hall formula, as given below and shown in figure 11

$$\beta \cos \theta = \frac{k\lambda}{L} + 4 \sin \theta,$$

where L is size of nanoparticle and θ is full-width half-maximum.

Figure 10. Topography spectrum of composite at 500°C.

Figure 11. Lattice strain of composite versus gelling time.

The AFM and XRD results show that increases in dislocation density in the heavily deformed regions cause a disintegration of the crystal into subgrains separated by low-angle grain boundaries, and rotation of subgrains to form nanograins with random orientation with respect to each other, as revealed in topography spectrum in figure 11. Figure 10 also shows that grain refinement proceeds by substantial increases in dislocation density, followed by the formation of subgrains with dense dislocation walls, and a gradual increase in subgrain boundary misorientation which eventually leads to the full evolution of ultrafine grains with decreased dislocation densities.

3. Conclusions

We found amorphous structure which shows no lattice mismatch at metal/metal boundaries. The residual stresses with Cr in the composite are even lower than that of composite without Cr nanoparticles, as revealed in the stress-strain diagrams. AFM images show that the nanocrystallization process of the Al composite proceeds via an initial increase followed by a subsequent decrease in dislocation density to form nano-grains with a dislocation-free interior.

We could also synthesize nanometallic composites which are beneficial for the crack splitting, boundaries toughening and stress relaxation. They can deflect the crack and reduce crack propagation because of the presence of the tough Al phase.

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