PROCESS OF OXIDE FILM FORMATION ON JOINT INTERFACE OF METAL AND GLASS①

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ABSTRACT

The growth of oxide films on 476 alloy, with a small amount of additive elements such as Si etc., oxidized in wet hydrogen atmosphere is some times accompanied by the formation of a great many whiskers. Typical form of whiskers grown on the oxide film is of flag pole type with a globe on its top. The pole is a spinel single crystal oxide (Fe,Mn) Cr_2O_4 and the globe is a metallic compound $(Ni,Fe)_xAl_y$ covered with protective Al, Si oxide layer. Nucleation of the metallic globe named white particlc is formed at the early stage of heating between 700℃ and 900℃. It seems to be extracted from the alloy matrix as a result of aluminium diffusion. Axial growth of pole begins at about 1150℃. It is supposed that the whisker grows at the root of a white particle and the interaction effect between the stress of oxide around the particle and the climbing motion of dislocation beneath the particle. If the alloy surface is covered uniformly with Cr_2O_3 as the inital oxide film, its final surface oxide film has no whiskers even after long time oxidation at higher temperature in hydrogen atmosphere. Proper surface treatment of base alloy, such mechanical brushing, is very effective for the formation of Cr_2O_3 at initial stage.it is supposed that the brushed surface may be activated to produce surface reactions by an enrichment of lattice defects.

Key words: sealing alloy, oxide film, oxide whisker

1 INTRODUCTION

The quality of hermetic sealing of metal in glass is enssential for the reliability and service life of electronic vacuum devices. To guarantee the sealing strength of dissimilar materials the property and the thickness of oxide film is very important in addition to the difference of thermal expansion coefficient which must be less than 10%. A transition layer of the sealing interface is needed to improve the sealing strength and the hermetic sealing.

Fe–Ni–Cr alloy (426 or 476 alloys) is used, for example, for the positive cap in the Braun tube of colour TV. In order to increase the sealing strength the alloy is oxidized in wet hydrogen to form an oxide film composed of corundum Cr_2O_3 and spinel (Fe, Mn)O.Cr_2O_3. An oxide whisker which often grows on the surface of oxide film looks like a layer of

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yellow powder. During sealing at high temperature in air, the yellow powder transfers to oxide of high valence and damages the sealed device due to the defect of nonuniformity in colour[1].

Every manufacturing technology of strip and positive cap has some influence on the amount of whiskers on the surface of oxide flim.

There are some papers about the formation mechanism of whisker[2]. But few papers on whisker growth on solids have been published and the mechanism is not yet clear. In this paper, the factors which influence the formation of oxide whiskes are examined. The formation mechanism and effect of small additive elements are discussed.

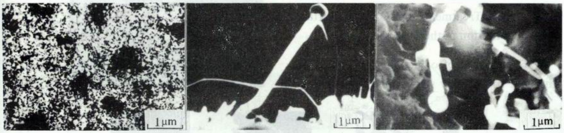
2 EXPERIMENTAL RESULTS

A NR476 alloy (Fe–Ni47–Cr6) strip of 0.35 mm or 0.5 mm in thickess was used. Positive caps were punched from an annealled strip at 1000℃ in hydrogen, cleaned and then oxided in wet hydrogen at 1200℃.

2.1 *The Morphology and Component of Oxide Whisker*

The appearance of oxide whisker on the surface is shown in Fig.1.

The whisker can be classified into 5 types:



a–distribution in group, b–flagpolc like, c–complicated shape

Fig.1 Appearance of oxide whisker

flagpole like needle with spherical or hexagon head (Fig. 1b), complicated shape needle with head (Fig. 1c)and so on. The diameter of the spherical head is from 0.2μm to 2.5μm. The thickness and length are 0.1—0.7μm and 0.5—10μm respectively. These oxide whiskers grow up from the surface of the alloy directly.

The components of oxide film:

Fig. 2 shows the distribution of elements in the transverse section of oxide film. It may be divided into two parts: an inter-oxide layer (alloy-interface) and a surface oxide film (interface-oxide). Cr-oxide is enriched near the interface in oxide film. Si-oxide is concentrated in the interface but Mn-oxide is on the surface of oxide film and Al-oxide is concentrated along the grain boundaries of the inter-oxide layer.

The oxide film is mainly composed of Cr_2O_3 (44wt%) and (Fe,Mn,Ni)Cr_2O_4 and inter oxide of alloy is of Al_2O_3. SiO_2. $(Cr,Al)_2O_3$. (Fe,Mn)Cr_2O_4.

The components of oxide whisker:

The oxide whisker is composed of (Mn, Fe,Ni)Cr_2O_3 (94wt%) with spinel type with the ratio of Fe: Mn: Ni is 44: 37: 19 and the distribution of elements is shown in Fig.3.

Ni and Fe are concentrated in the head of the whisker and Cr, Mn and Fe are enriched in the body.

The results of TEM and ESCA show that there exists a shell on the surface of the head of the whisker with a thickness of about 100A, which composed of amorphous SiOx and complex oxide of Al and Mn. Inside the head of the whisker there is a $(Ni,Fe)_3Al$ intermetallic compound with d(111) = 2.09A, d(200) = 1.82A,

The direction of the head along the axis of the whiskers' body is [111] (Fig.4).

The body of the whisker is composed of a single crystal of (Fe, Mn) Cr_2O_4 and its axis is [132].

2.2 *The Eff ect of Pre-treatment on the Formation of Yellow Powder*

2.2.1 Heat Treatment and Original Surface Condition of the Strip

The amount of oxide whisker formed on the cold rolled alloy strip which is treated by oxidation is small (G_2 or G_3) (G presents the degree of whisker). The amount of whisker increases when the strip is pre-annealled at 900℃ in hydrogen and then oxidized. The increase of the whisker amount depends on the point of the used hydrogen.

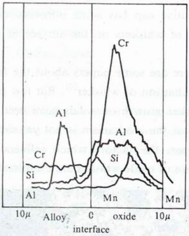


Fig.2 The distribution of elements in the transverse section of oxide

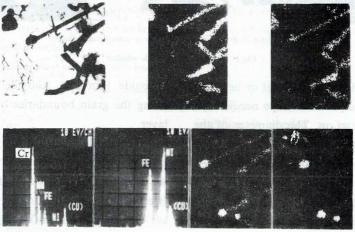


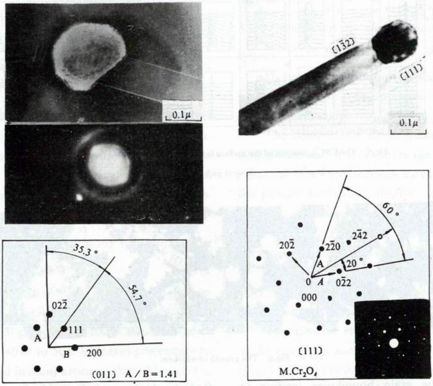
Fig.3 The distribution of elements in the head and in the body of a whisker.

The whiskers, as needles in groups, appear along the grain boundaries. Cr is enriched on the surface of the film oxide of cold-rolled strip. For pre-heat treatment strip, Al, Fe and Ni is segregated to the grain boundaries where they easily diffuse to the surface and form a lot of circular white particles whose main composition is Ni, Fe, Al and Si. These white particles might be the nuclei of whisker oxide.

Acid picking can not reduce the amount of whiskers, but surface grinding and strain forced on the surface are useful to reduce the amount of the whiskers (From G_6 to G_2).

2.2.2 The Change in Oxide Film During the Increase of Temperature

The specimens cut from a cold-rolled strip, grided or strained strip were heated from 200℃ to 900℃ in wet hydrogen and then cooled rapidly. We found no circular white particles formed on the surface of the oxide film. The colour of the surface changed from gold yellow at 500℃ to red-brown at 900℃. The oxide film is composed mainly of Cr_2O_3.



a)head b)body

Fig.4 TEM observation of the head and the body of a whisker

A lot of white particles appear on the surface of pre-annealled specimens after heating from 600℃ to 900℃. These white particles are removed by acid pickling, but they appear again when heated above 650℃. These particles are composed of Al_2O_3, SiOx (amorphous), Cr_2O_3 and complex oxide of Fe and Ni (Fig. 5).

The results illustrate that at first Al and Ni diffuse to the surface to be oxidized. A low melting mixture is formed by Al_2O_3 and SiO_2 combined with complex oxide of Fe and Ni.

The ESCA analysis of oxide film specimens which were heated at 1000—1250℃ in wet hydrogen (D.P. 35℃) shows that the oxides grow up and the surface shell thickens. Mn diffuses more rapidly and complex oxides are formed. At 1150℃ some needles with spherical heads grow out from part of the white particles. At 1200℃ the amount of these needles increases and they grow into whiskers with the increase of time (Fig.6).

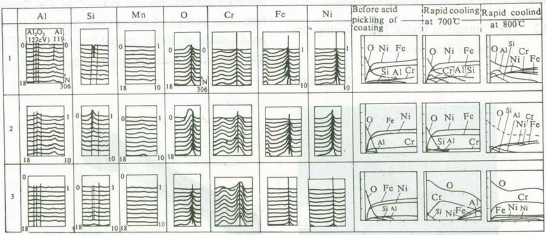


Fig.5 The ESCA analysis of the surface layer of specimens cooled from 900℃

1—pre-annealled; 2—acid pickling; 3—ground strip

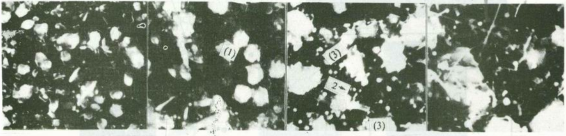


Fig.6 The growth of whiskers

Near the grain boundaries tending to form whiskers, the Mn content is high. The white oxide (1) is (Ni, Fe, Mn) $(Cr, Al)_2O_4$. The small circular white particles (2) are (Ni, Fe, $Cr)_3Al$ and Al_2O_3,SiO_2, which may be the heads of whiskers. The white elongated particles(3)are (Fe, Mn, $Ni)Cr_2O_4$, which may be the body of whiskres. The region void of white particles is covered by Cr_2O_3 film.

2.2.3 Pre-treatment at High Temperature

The degree of whisker amount is redueed from G_6 to G_2 and the oxide film is mainly composed of Cr_2O_3 and (Fe, $Mn)Cr_2O_3$ for pre-heated the specimens at 1200℃ for 10 min in hydrogen(D.P.—70℃).

In these specimens a rich Cr band appears near the grain boundaries enriched by Al. It might control the segregation of Fe and Ni to the grain boundaries and reduce the amount of low melting point mixture.

Deposition of Cr, Al or Zr: There are no whiskers formed on the specimens which are deposited by Cr, Al or Zr in vacuum and then oxidized at 1200℃ (D.P.35℃). In this case the surface is covered by Cr_2O_3.

Addition of elements: Trace elements of Zr, Hf, Y, B or Ca are added into the NR 476 alloy. It can restrain the formation of whiskers (G_5–G_2) and make the oxide film more compact.

Adding Zr or Hf can reduce the grain size of the alloy and the oxidation velocity and can enhance the inter-oxidation, so the strength between oxide film and alloy is increased.[3–5]

3 DISCUSSION OF THE FORMATION MECHANISM OF WHISKERS

The formation of oxide film and whiskers with heads is controlled by diffusion, nucleation and growth. They depend on the structure of oxide film, the alloying elements, grain boundaries, stress condition and the atmosphere.

3.1 *The Formation Process of Whiskers on Oxide Film*

In the initial stage of oxidation the sequence of element oxidation depends on its dissociation presure. At 1000℃ in wet hydrogen(D. P. 40℃ to 50℃)Al takes precedence to be oxidized in comparsion with Si, Mn and Cr. The density of alloy defects caused by cold rolling, grinding and straining is useful for forming Cr_2O_3 film on the surface. It is impossible to grow uniform Cr_2O_3 film. On the surface of a dry hydrogen annealled and acid pickled alloy, Al is oxidized along the grain boundaries, near which Ni and Fe are enriched and they combine with Al to form a low melting mixture, composed of $(Ni, Fe)_xAl_y$ and $(Al, Si, Mn)_xO_y$, which consists of white particles formed above 650℃. The surface layer of these white particles is composed of SiO_2, Al_2O_3 or MnO, which are the heads of whiskers.

In the later stage as Cr oxidized, the Cr content at the interface of the alloy with oxide film decreased, so Cr, Mn and Fe diffuse. On the surface, $(Fe, Mn)Cr_2O_4$ with spinal type is formed. The component of oxide film is composed of inter oxide layers Cr_2O_3 and $(Fe, Mn) Cr_2O_3$ by which the white particles are surrouned.

3.2 *Explanation of the Formation of Whiskers.*

During the formation of oxide film at high temperature a compressive stress on the alloy surface occurs.

The compressive stress creates a dislocation source and it accelerates the diffusion of elements. Screw dislocations move upward and the process acceblerates the Fe and Ni to migrate to the white particles, so the whiskers grow out. The growth of whiskers cause the compressive stress to be relieved[6–8].

During growth, some whiskers keep a spiral character. Their appearance is polygonal rather than cylindrical.

The increase of compressive stress in the oxide film enhances the growth of whiskers (Fig, 7) and the amount of whiskers formed on annealled strips is greater than that on cold rolled strips and ground strips.

It is difficult to explain the formation of a single whisker crystal on the oxide film in NR476 alloy according to the VLS model proposed by Wager.

So a SCS (solid-chemistry-solid) or SS (solid-solid) model is put forward tentatively. Selective diffusion of some elements, chemical reaction and then directional growth by diffusion in solid are processed, and the structure scheme is shown in Fig.8.

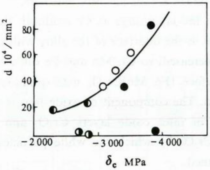


Fig.7 The dependence of the density of whiskers on the compresive stress

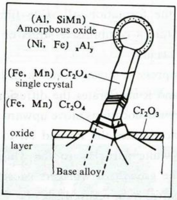


Fig.8 The schematic structure of a whisker

4 CONCLUSION

1 In the initial stage a uniform and dense Cr_2O_3 film is first formed on the surface. This Cr_2O_3 film controls the formation of whiskers, while the oxidation atmosphers is controlled and the surface of alloy is active.

2 In the initial stage, being lack of compresive stress on the surface of annealled alloy the white particles are easily formed near the grain of boundaries. The white particles are whisker nuclei, which are composed of a low melting mixture covered by a shell of amorphous SiO_2 and Al_2O_3.

3 The body and the root of whiskers are composed of single crystal $(Fe,Mn)Cr_2O_4$ with quardrilateral type and $(Fe, Mn)Cr_2O_4$ with spinal type respectively.

4 Pre-addition of compressive stress, controlling of the dew point of hydrogen and temperature, addition of alloying elements and the deposit of Cr, Al, Zr are useful to prevent the formation of whiskers.

5 A SS model is put forward tentatively to explain the formation of whisker during oxidation of the alloy.

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