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High temperature oxidation behavior of magnetically sputtered Ni-0.5Y micro-crystal coating

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Abstract: The isothermal and cyclic oxidation behaviors of bulk pure nickel and its magnetically sputtered Ni-0.5Y micro-crystal coating were studied at 1 000 ℃ in air. Scanning electronic microscopy (SEM) and transmission electronic microscopy (TEM) were used to examine structures of the coating and the NiO oxide films. Laser Raman spectrum was also used to measure the stress level in NiO films formed on bulk nickel and the coating. It was found that Ni-0.5Y micro-crystal coating had lower oxidation rate, and the grain-size of NiO formed on Ni-0.5Y coating was also relatively smaller than that formed on bulk nickel. Meanwhile, the compressive stress level of oxide film formed on Ni-0.5Y coating was lower than that formed on bulk nickel, and the oxide film's high temperature plasticity was improved in the coating case. The improvements of anti-oxidation properties of the sputtered Ni-0.5Y coating were due to the micro-crystal structure and the rare earth element Y.

Key words: magnetic sputtering; oxidation; Laser Raman; yttrium

The resistance of high temperature coatings to oxidizing environment depends on the formation of slowly growing and adherent oxide films, and among these coatings, magnetically sputtered metallic coatings such as the MCrAl-type coatings are the most commonly used[1-3]. Usually, the addition of a small amount of rare earth element will remarkably improve the coating's anti-oxidation property; nevertheless the rare earth effect and mechanism have not yet been fully understood. In this paper, a magnetically sputtered Ni-0.5Y coating was prepared on a bulk pure nickel substrate to study the relationship between the coating's oxidizing property and its micro-structure as well as the yttrium effect.

1 Experiment

Pure (99.94%) bulk nickel was wire-cut to 15 mm × 10 mm × 2 mm samples which were ultimately polished by 0.2 μm Al_2O_3 abrasive paste. After being ultrasonically cleaned in acetone and alcohol, some specimens were magnetically sputtered with a Ni-0.5Y coating in the SBH-5115D magnetic sputtering machine with a sputtering voltage of 558 V and the sputtering current of 5.03 A. The thickness of the coating is about 10 μm which was monitored in-situ and controlled by an FTM-3C quartz-crystal thickness monitor.

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Then pure nickel sample and the Ni-0.5Y coating sample were isothermally oxidized at 1 000 ℃ in air for about 50 h, and the SETTRAM-50 thermal balance was used to record the mass-gain curves of both samples. After isothermal oxidation, the morphologies of NiO oxide films formed on both samples were examined in scanning electronic microscopy (SEM). A pure nickel sample and the Ni-0.5Y coating sample were also cyclically oxidized at 1 000 ℃ in air for 90 h (50 min heating + 10 min cooling) and the mass-change curves of both samples were recorded. After cyclic oxidation, SEM was then used to examine morphologies of the oxide/substrate and oxide/coating cross-sections of the two samples.

In Laser Raman, a Hitachi RM-200 Raman spectrum with an Ar^+ laser tube was used to measure the stress level in oxide films, and the Raman peak was calibrated to ± 0.2 cm^{-1} accuracy.

2 Results and Discussion

The scanning electronic microscopy (SEM) image and transmission electronic microscopy (TEM) bright field image of magnetically sputtered Ni-0.5Y coating before oxidation were shown in Fig.1(a) and Fig. 1(b), respectively. The sputtered coating had a homogeneous structure, and from the TEM image (Fig. 1(b)) we found that the actual grain-size in Ni-0.5Y coating was within 50 nm to 500 nm, much smaller than the overall SEM image as shown in Fig.1(a). Meanwhile, there were many micro-cracks existing

between the sputtered grains. These micro-cracks mainly came from the sputtering and depositing process.

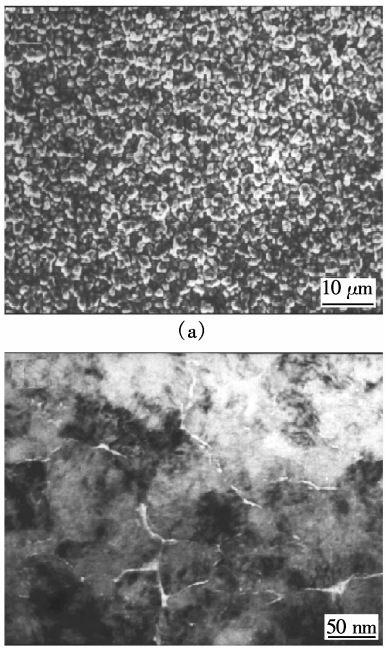

Fig.1 Surface SEM morphology and TEM bright field image of Ni-0.5Y coating

The isothermal oxidation mass-gain curves of pure nickel and sputtered Ni-0.5Y coating at 1 000 ℃ were shown in Fig.2. We can see that the Ni-0.5Y coating and the substrate nickel both showed parabolic-type oxidation, while the former had a much lower oxidizing rate than the latter.

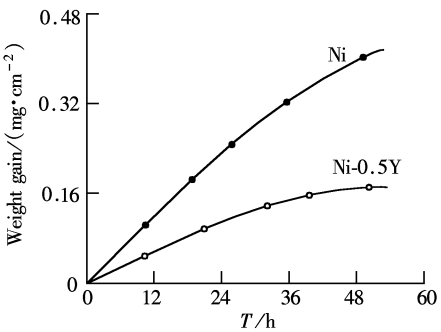

Fig.2 Isothermal oxidation mass gain curves of bulk nickel and Ni-0.5Y coating

Fig.3 shows the SEM morphologies of oxide films formed on bulk nickel (Fig.3(a)) and Ni-0.5Y coating (Fig.3(b)) after 50 h isothermal oxidation in 1 000 ℃ air. Severe cracking and spallation have occurred in NiO film formed on bulk nickel, while the NiO film formed on Ni-0.5Y coating remained intact and adherent. The grain size of NiO oxide formed on Ni-0.5Y coating was also much smaller than that formed on bulk nickel.

The reason for the Ni-0.5Y coating's relatively

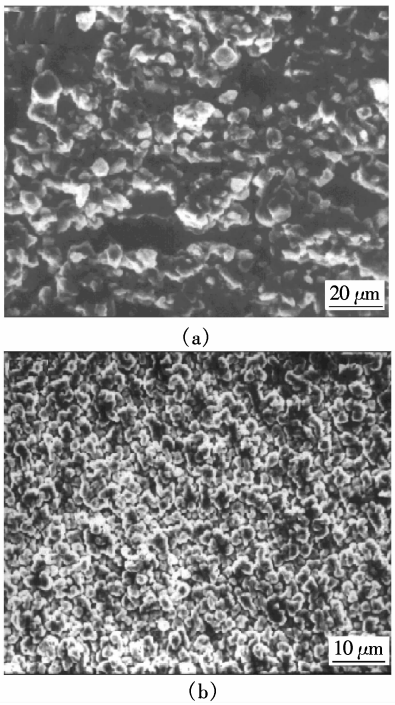

Fig.3 SEM morphology of oxide films formed on bulk nickel and Ni-0.5Y coating in isothermal oxidation

lower oxidizing rate was mainly due to the addition of rare earth yttrium. At the initial oxidizing stage, yttrium was quickly oxidized because of its rather high chemical activity. These Y-containing oxides then dispersed at NiO grain boundaries in the form of rather fine particles (e.g., Y_2O_3 or NiY_2O_4 spinel) and inhibited the Ni^{2+} and O^{2-} ion diffusion process within oxide film, hence remarkably lowering the coating's oxidizing rate. The authors[4,5] used high resolution electronic microscopy (HREM) to study the Cr_2O_3 film growing on Co-40Cr binary alloy which was ion-implanted with yttrium, a similar rare earth effect was found along with the dispersion of fine Y_2O_3 particles at Cr_2O_3 grain boundaries. Other researchers[3,6] found that yttrium could also exist in the form of Y^{3+} ions at grain boundaries, and inhibit the cation and anion diffusion within oxide films. Further work still needs to be done under field emission electronic microscopy (FEEM) equipped with high resolution energy dispersion spectrum (EDS).

Fig.4 shows the cyclic oxidation mass-change curves of bulk nickel and Ni-0.5Y coating at 1 000 ℃. We could find that the oxide film formed on bulk nickel began to spall and show weight-loss after 20 h cyclic oxidation, while no weight-loss was found on the Ni-0.5Y coating sample during the whole 90 h cyclic oxidation.

SEM morphologies of cross-sections of the bulk

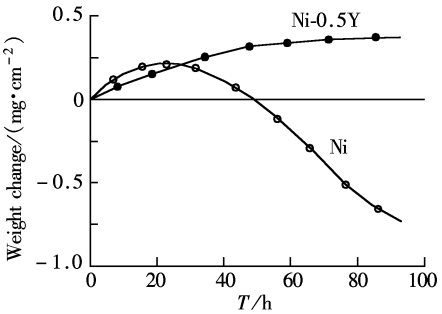

Fig.4 Cyclic oxidation mass change curves of bulk nickel and Ni-0.5Y coating

nickel sample and the coating sample after 90 h cyclic oxidation are shown in Fig.5. We could see that severe cracking and spallation had occurred at the NiO/Ni interfaces (see Fig.5(a)), while no noticeable cracking or detachment could be seen at the NiO/Ni-0.5Y/Ni interfaces (see Fig.5(b)). The cyclic oxidation results show that the magnetically sputtered Ni-0.5Y coating and its NiO oxide film had very good anti-thermal-shock property.

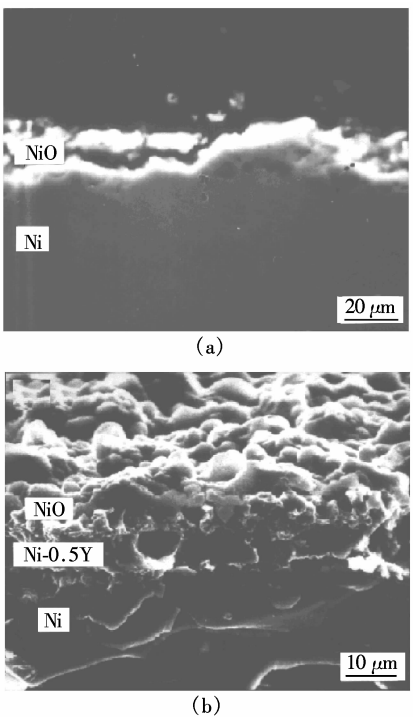

Fig.5 SEM morphology of cross-sections of bulk nickel and Ni-0.5Y coating in cyclic oxidation

When a monochromatic laser light was shed on a solid sample, the laser light is inelastically scattered to give a Raman peak which corresponds to the particular lattice vibration of the solid. If the solid was stressed, the vibrational frequency of the Raman peak would shift to a higher frequency for compressive stress and to a lower frequency for tensile stress, and this could be used to measure the internal stress level of the solid. In our experiment, fine NiO powders were annealed at 850 ℃ for 40 h to release the possible internal stress, and were considered as the standard stress-free NiO samples. Then Raman spectrums were examined on NiO oxide films formed on bulk nickel and Ni-0.5Y coatings which were isothermally oxidized for 50-hour, along with the standard NiO powders, the results are shown in Fig.6.

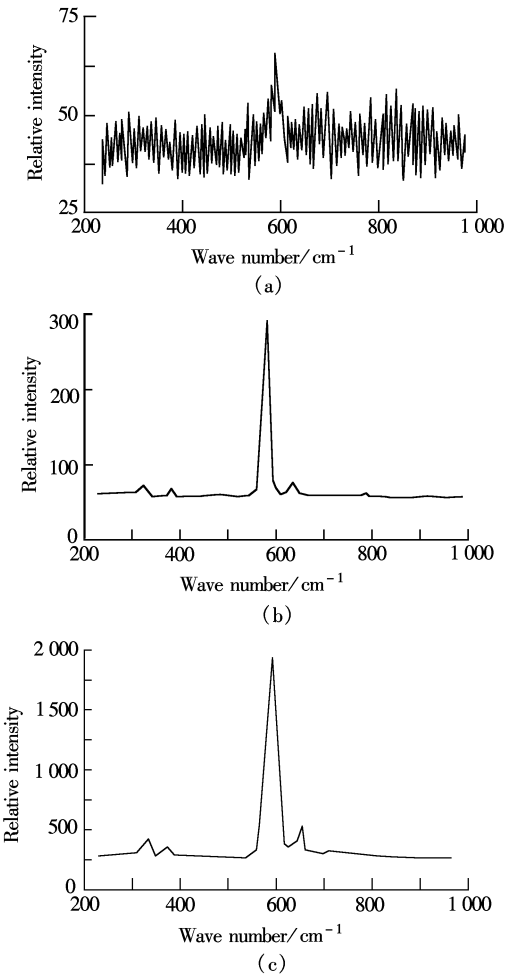

Fig.6 Laser Raman stress measure results. (a) Raman spectrum of standard NiO Powder; (b) NiO oxide films formed on bulk nickel; (c) Ni-0.5Y coating

According to Birnie[6], there was a linear relationship between the internal stress level and the Raman peak shift. From Fig.6 we can see that the NiO film formed on Ni-0.5Y coating had lower compressive stress than that formed on bulk nickel.

Usually the internal stress in oxide film includes the growing stress and the thermal stress. The former comes from the volume difference between the oxide formed and the metal consumed, and the latter comes from the thermal expansion difference between the oxide and the metal substrate[7,8]. On one hand, NiO film formed on Ni-0.5Y coating had lower growing speed than NiO film formed on bulk nickel (see Fig.

2), which meant the growing stress in the former was less than that in the latter. On the other hand, NiO film formed on Ni-0.5Y coating had a much smaller grain size (see Fig.3), the compressive stress in the oxide film could be partly released via high temperature creeping of NiO grains; while the compressive stress in NiO film formed on bulk nickel could be released only in transient forms, such as cracking or spalling of the film. This could be confirmed by the Laser Raman stress-measure results (see Fig.6) and the SEM morphologies of surface films (see Fig.3 and Fig.5). The authors[5] had used the acoustic emission (AE) method to study the cracking and spalling process of Cr_2O_3 oxide film formed on Co-40Cr alloy, similar grain-size reducing effect and stress reducing effect has been found in Cr_2O_3 film due to yttrium ion-implantation of the alloy.

Meanwhile, there were many micro-cracks existing in the Ni-0.5Y coating (Fig.1(b)). Due to the magnetic sputtering process, these pre-existing micro-cracks might help relieve the growing stress and the thermal stress of the NiO film during the subsequent oxidizing process. Further studies on this aspect are still needed.

3 Conclusions

1) The magnetically sputtered Ni-0.5Y micro-crystal coating had a lower oxidizing rate than its substrate nickel; the surface NiO oxide film had a much smaller grain size and was more adherent than that formed on bulk nickel.

2) The NiO oxide film formed on Ni-0.5Y coating had better high-temperature plasticity and anti-thermal-shock property than that formed on bulk nickel.

3) The Ni-0.5Y coating's good anti-oxidation properties can be primarily attributed to its lower internal compressive stress level and the addition of rare earth yttrium.

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磁控溅射 Ni-0.5Y 微晶涂层高温氧化行为研究

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摘 要 研究了纯镍及其表面磁控溅射 Ni-0.5Y 微晶涂层在 1 000 ℃空气中的恒温氧化和循环氧化行为.通过扫描电镜(SEM)和透射电镜(TEM)对涂层以及表面 NiO 氧化膜的形貌和结构进行了研究.此外,用激光拉曼(Raman)谱对 2 种样品表面 NiO 氧化膜内应力大小进行了测量,结果表明:Ni-0.5Y 微晶涂层与基体镍相比有更低的氧化增重速率, 表面 NiO 氧化膜的晶粒尺寸明显减小, 膜的高温塑性得以改善.同时, 氧化膜内的压应力水平也有所降低, 因而改善了 NiO 氧化膜的粘附性和保护性.磁控溅射涂层的微晶结构以及稀土元素钇的存在均有助于提高涂层的抗高温氧化性能.

关键词 磁控溅射; 氧化; 激光拉曼; 钇

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