

The Effect of Nanocrystallization on the Selective Oxidation and Adhesion of Al_2O_3 Scales

Fuhui Wang*

Received September 9, 1996; revised December 12, 1996

Many mechanisms for the effect of reactive elements on the selective oxidation and scale adhesion of alloys have been proposed. However, nanocrystallization (or microcrystallization) has recently been found to have almost the same effect as that of reactive elements. This note reviews the effect of nanocrystallization on the selective oxidation and adhesion of Al_2O_3 scale with particular reference to the author's own results.

KEY WORDS: nanocrystallization; oxidation; mechanism.

INTRODUCTION

The formation of a stable and slowly growing protective oxide scale such as Al_2O_3 , Cr_2O_3 , or SiO_2 is essential for alloys used at high temperatures. However, the protective Al_2O_3 scales formed at high temperatures may be prone to crack and spall during thermal cycling. Therefore, a suitable technique to enhance adhesion of Al_2O_3 scales, so that alloys and coatings can resist high temperatures, has become a major focus of high-temperature-materials research. To date, the most successful technique is to add a small amount of reactive elements such as Y, Ce, Hf, etc., or their oxides to the alloy. The mechanisms of this reactive-element effect in promoting scale adhesion have been reviewed by many researchers.¹⁻⁴

Recently, it has been found that the oxidation resistance of superalloys is improved through nanocrystallization (or microcrystallization). In this

*State Key Laboratory of Corrosion and Protection, Institute of Corrosion and Protection of Metals, Academia Sinica, Shenyang 110015, China.

paper, the effects of nanocrystallization on the selective oxidation and adhesion of Al_2O_3 scales of alloys with particular reference to the present author's own research are reviewed.

EFFECT ON SELECTIVE OXIDATION

The oxidation resistance of an alloy depends on the stability and growth rate of the oxide formed on the surface and the concentration of the oxide-forming constituent in the alloy. If the concentration of the oxide-forming constituent is below a critical amount, internal oxidation is observed. According to Wagner,⁵ the critical solute concentration for the transition from internal to external oxidation has been expressed as

$$N_B = \left(\frac{\pi g^* N_O D_O V_M}{2 D_B V_{OX}} \right)^{1/2} \quad (1)$$

where $N_O D_O$ is the oxygen permeability in A , D_B is the solute diffusivity, g^* is a factor determined by the volume fraction of oxide required for the transition, and V_M and V_{OX} are the molar volumes of the alloy and oxide, respectively.

Therefore, the solute concentration of the oxide-forming constituent in an alloy should be greater than N_B in order to form a continuous external scale. Nanocrystallization provides two significant contributions to the formation of an external oxide scale. The first is to increase the number of possible nucleation sites of oxide due to an increased concentration of grain boundaries on the alloy surface.⁶ The second is to increase the diffusivity of solute (D_B) in the alloy as a result of grain-boundary diffusion.⁷ For example, cast K38G alloy containing about 3.5–4 wt.% Al and 16 wt.% Cr forms Cr_2O_3 scale (Fig. 1a), while its sputtered microcrystalline coating with the

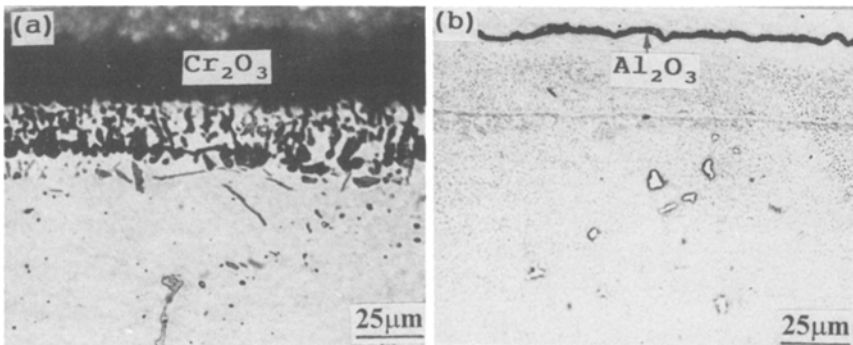


Fig. 1. Optical micrographs of cross-sections of specimens oxidized at 1000°C: (a) cast K38G alloy for 200 hr; and (b) K38G nanocrystalline coating for 500 hr.

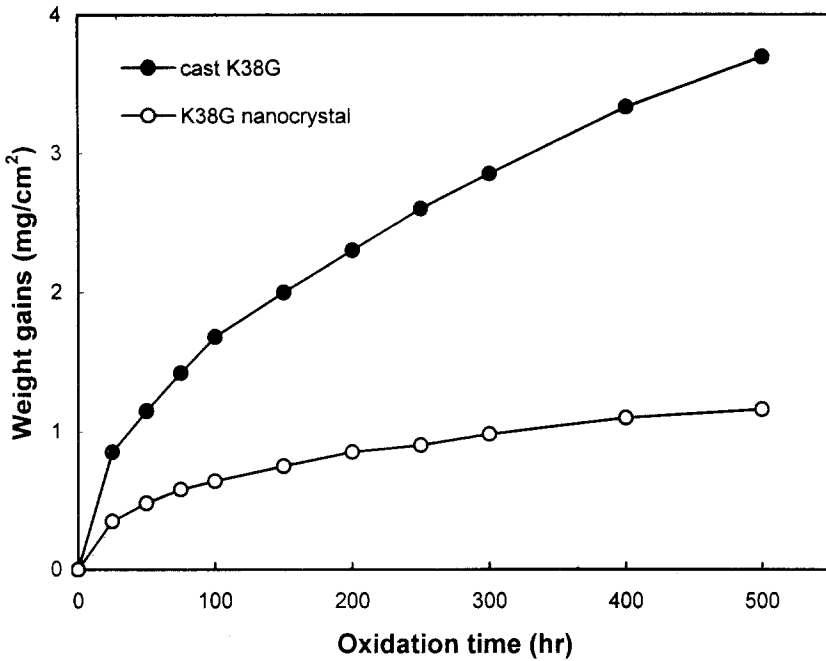


Fig. 2. Oxidation kinetics of cast K38G alloy and its nanocrystalline coating at 1000°C.

same composition as the cast alloy forms as Al₂O₃ scale (Fig. 1b).⁸⁻¹⁰ Therefore, nanocrystallization decreases the critical aluminum content in K38G alloy to form an external Al₂O₃ scale, in effect changing the alloy from a chromia-former to an alumina-former, with a corresponding improvement in the oxidation resistance (Fig. 2).¹¹ For K17F alloy¹² and Ni₃Al intermetallic compound,¹³ it has been observed that nanocrystallization provides the same effect.

Hence, it can be shown that nanocrystallization, due to increasing D_B , can decrease the critical solute concentration of the alloy required to form a continuous external scale. The relationship between the critical solute concentration (N_B) and grain diameter (d) is derived as follows. For the nanocrystalline compounds, an effective diffusivity (D_{eff}) should be substituted for the solute diffusivity D_B . Assuming that the grain structure of the alloy parallel to the surface can be expressed using Fig. 3, the area of grain (A_b) and grain-boundary (A_{gb}) for one grain can be calculated as follows

$$A_b \approx \frac{\sqrt{3}}{2} (d - \delta) d \quad \text{and}$$

$$A_{gb} \approx \sqrt{3} d \cdot \delta$$

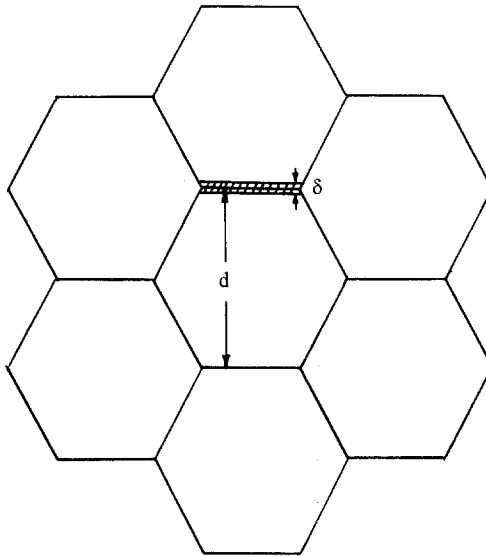


Fig. 3. Schematic diagram of grain structures of the alloy parallel to the surface.

where d is the grain diameter and δ is the grain-boundary thickness. D_{eff} is determined by

$$\begin{aligned}
 D_{\text{eff}} &= \frac{D_{gb} \cdot A_{gb} + D_b A_b}{A_{gb} + A_b} \\
 &= \frac{\sqrt{3}d \cdot \delta \cdot D_{gb} + \frac{\sqrt{3}}{2} (d + \delta)d \cdot D_b}{\sqrt{3}d \cdot \delta + \frac{\sqrt{3}}{2} (d - \delta)d}
 \end{aligned} \quad (2)$$

where D_{gb} and D_b are the grain-boundary and bulk-diffusion coefficients of the solute, respectively.

Considering the following two limiting conditions:

- (1) $\delta/d \sim 0$ (single crystal or large-grain polycrystal), Eq. (2) can be simplified as

$$D_{\text{eff}} = D_b \quad (3)$$

- (2) $\delta = d$ (the whole material is composed of boundaries), Eq. (2) can be simplified as

$$D_{\text{eff}} = D_{gb} \quad (4)$$

For the sputtered nanocrystals ($d=20\text{--}100\text{ nm}$), grain-boundary diffusion predominates, while the grain-boundary thickness $\delta \approx 1\text{ nm}$ and $\delta/d \ll 1$. Equation 2 can be simplified as

$$D_{\text{eff}} = \frac{2\delta}{d} \cdot D_{gb} \quad (5)$$

Introducing D_{eff} into Eq. (1) instead of D_B and assuming that nanocrystallization does not affect oxygen permeability ($N_O D_O$) then Eq. (1) can be simplified as

$$N_B = K \cdot \sqrt{d} \quad (6)$$

where K is a constant. From Eq. (6), it is seen that the critical solute concentration is directly proportional to the square root of the grain diameter. It should be noted that this equation has two prerequisites, the first is that grain-boundary diffusion predominates in the materials and the second is that the grain size does not affect the oxygen permeability. However, the effect of nanocrystallization on selective oxidation of aluminum in a Ti–Al binary alloy is not obvious.¹⁴ The reason may be that nanocrystallization equally enhances the rate of diffusion for both titanium and aluminum.

EFFECT ON SCALE ADHESION

The above discussion theoretically demonstrates the effect of nanocrystallization on the transition of alloys from internal to external oxidation. However, for the alloys which already form a continuous Al₂O₃ scale such as Co–30Cr–5Al,^{15–17} and Ni₃(AlCr)^{18–19} alloys, the only difference is that the scale formed on the normal grain-size alloy tends to spall, while the scale formed on nanocrystalline coatings is very adherent (Fig. 4). Therefore, there is a pronounced effect of nanocrystallization on scale adhesion. It is acknowledged that scale adhesion is dependent upon two factors: (1) stresses in the scales and (2) the bonding between the scale and the substrate. Both factors can be affected by nanocrystallization.

Effect on Thermal Stress in Oxide Scales

The thermal stress of the oxide scale formed on the metallic substrate can be calculated by

$$\sigma_{th} = \frac{E_{OX} \Delta \alpha \Delta T}{1 - \nu_{OX}} \quad (7)$$

where E_{OX} is Young's modulus of the oxide, $\Delta \alpha$ is the difference in thermal expansion coefficients between the metallic substrate and the oxide scale,

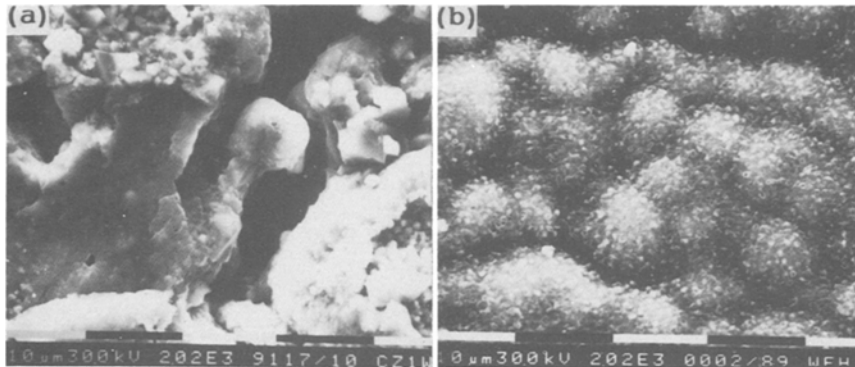


Fig. 4. SEM surface morphologies of cast Co-30Cr-5Al (a), and its nanocrystalline coating (b) after 100 cycles of oxidation at 1000°C.

ΔT is the temperature change and ν_{OX} is Poisson's ratio of the oxide. As the grain size of oxide scale formed on the nanocrystalline material is much smaller than that formed on the as-cast alloy¹⁷ and given that the grain boundaries in nanocrystalline alloys have a much larger thermal expansion coefficient (2.5–5 times) than the crystal,²⁰ the oxide scale formed on nanocrystalline materials has a larger thermal coefficient than that on the cast alloy. Therefore, the thermal stress in the scale formed on nanocrystalline materials should be less than those in the scale of the cast alloy.

Effect on Stress Relief

Two mechanisms exist to relieve the stresses in the oxide scale without failure, plastic deformation of (1) the scale, and of (2) the substrate metal. Any factor which enhances the plastic deformation of the scale and/or the substrate can reduce the stresses in the scale. According to the diffusional-creep theory, the deformation rate, $\dot{\epsilon}$, of a polycrystalline material at low temperature when grain-boundary diffusion predominates is²¹

$$\dot{\epsilon} = \frac{B\sigma\Omega\delta D_{gb}}{d^3KT} \quad (8)$$

where B is a numerical constant, σ is the tensile stress, Ω is the atomic volume, d is the average crystal size, D_{gb} is grain-boundary diffusivity, δ is the thickness of the boundary, K is Boltzmann's constant and T is temperature, °K.

According to Eq. (8), the diffusional creep rate of the scale can be enhanced by reducing the grain size of the scale. Thus, the scale formed on

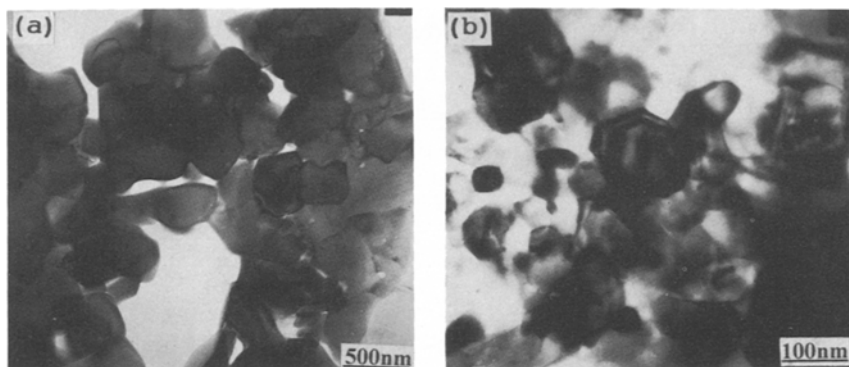


Fig. 5. TEM bright-field images of oxide scales formed on cast Co-30Cr-5Al (a) and its sputtered microcrystalline coating (b) after 50 hr oxidation at 1000°C.

the nanocrystalline coating is much finer than that formed on the cast normal, grain-size alloy (Fig. 5)¹⁷ and that on the aluminide coating,¹⁰ therefore the growth and thermal stresses may be partially relieved by plastic deformation of the scale. Moreover, deformation of the metallic substrate of nanocrystalline coatings is much easier than deformation of the as-cast alloy, which may play an important role in relieving the oxide stresses during thermal cycling. Tedmon,²² studied the effect of Cr content on the oxidation resistance of Fe-Cr alloys and found that the scale-spalling tendency increases with increasing Cr content due to the rapid increase of the alloy strength. It is suggested that the Fe-rich alloys have more resistance to spalling because their relative lack of high-temperature strength permits them to accommodate by plastic deformation. These results support the hypothesis that stress relief by plastic deformation of the metal adjacent to the scale is an important factor in preventing or reducing spalling. Stress generated under isothermal conditions is relieved by plastic deformation of both the scale and the metal. During cooling, the yield strength of the oxide increases and the scale is no longer capable of relieving the stress by flow. The stress relief will depend on the capability of the metal adjacent to the scale to flow.

The above discussion demonstrates that theoretically the stresses of scales formed on the nanocrystalline coatings should be lower than those formed on coarse-grain alloys, due to enhanced plastic deformation of the scale and the substrate.

Effect on Bonding Force

The sputtered coatings possess columnar structures, and oxidation along columnar grains can form many micro-pegs (Fig. 6),¹⁹ which anchor

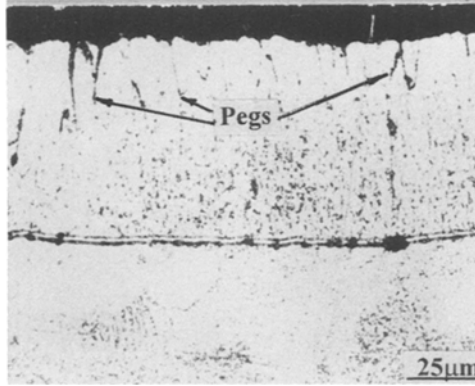


Fig. 6. Cross-section of Ni₃ (AlCr) nanocrystalline coating after 200 hr oxidation at 900°C showing the pegs.

the scale to the substrate. Assuming that the oxide scale is anchored to the substrate only by the pegs formed along grain boundaries into the alloy, the bonding force between the oxide scale and the substrate is directly proportional to the ratio of grain boundaries per unit area (R_{gb}) on the alloy surface. According to Fig. 3, R_{gb} can be calculated by

$$\begin{aligned}
 R_{gb} &= \frac{A_{gb}}{A_{gb} + A_b} \\
 &= \frac{\sqrt{3}d \cdot \delta}{\sqrt{3}d \cdot \delta + \frac{\sqrt{3}}{2}(d - \delta)d} \\
 &= \frac{2\delta}{d + \delta} \\
 &\approx \frac{2\delta}{d}
 \end{aligned} \tag{9}$$

Thus, the bonding force of the scale is inversely proportional to the grain size. Therefore, since the grain size of the nanocrystalline coating is several orders of magnitude smaller than that of the normal grain-size alloy, the bonding force of the scale formed on the nanocrystalline coating is much greater than that on the normal grain-size alloy. This may account for the excellent adhesion of the scale formed on the nanocrystalline coating.

It should be noted that all papers dealing with the effect of nanocrystallization on oxidation resistance of alloys discussed here refer to

“sputtered” nanocrystalline coatings. Further studies are required to determine whether the nanocrystalline materials obtained using other methods follow the same behavior.

CONCLUSIONS

Nanocrystallization provides two beneficial effects on the oxidation resistance of alloys:

1. Promotes selective oxidation: A significant amount of grain boundaries exist on the alloy surface and substrate, which can act as nucleation sites for scale growth, and enhance the diffusion of Al from substrate to the surface, allowing the selective oxidation of aluminum, resulting in a continuous Al₂O₃ scale. This significantly enhances the oxidation behavior of the alloy.

2. Enhances scale adhesion: Nanocrystallization can enhance Al₂O₃ scale adhesion due to: (1) reducing the thermal stress; (2) relieving growth stresses and thermal stresses by enhancing plastic deformation of the scale and the substrate, and (3) increasing the bonding force between the scale and the substrate due to the formation of oxide intrusions into the substrate grain boundaries, which act as pegs, anchoring the scale to the substrate.

ACKNOWLEDGMENTS

The work was supported by the National Natural Science Foundation of China (NSFC) for the Outstanding Young Scientists and President's Special-Fund of The Chinese Academy of Sciences.

REFERENCES

1. D. P. Whittle and J. Stringer, *Phil. Trans. R. Soc. London, Ser. A*, **285**, 309 (1980).
2. F. H. Stott and G. C. Wood, *Mater. Sci. Eng.* **87**, 261 (1987).
3. A. M. Huntz, *Mater. Sci. Eng.* **87**, 251 (1987).
4. P. Y. Hou and J. Stringer, *Mater. Sci. Eng.* **A202**, 1 (1995).
5. C. Wagner, *Z. and Electrochem.* **63**, 772 (1959).
6. J. Stringer, *Oxid. Met.* **5**, 59 (1972).
7. C. S. Giggins and F. S. Pettit, *Trans. TMS-AIME* **245**, 2495 (1969).
8. H. Lou, F. Wang, B. Xia, and L. Zhang, *Oxid. Met.* **38**, 299 (1992).
9. H. Lou, S. Zhu, and F. Wang, *Oxid. Met.* **43**, 317 (1995).
10. H. Lou, F. Wang, S. Zhu, B. Xia, and L. Zhang, *Surf. Coat. Technol.* **63**, 105 (1994).
11. F. Wang, *High-Temperature Microcrystalline Coatings*, PhD dissertation, Institute of Corrosion and Protection of Metals, Academia Sinica (1992).
12. H. Lou, Y. Tang, X. Sun, and H. Guan, *Mater. Sci. Eng.* **A207**, 121 (1996).
13. F. Wang, H. Lou, and W. Wu, *Oxidation resistance of sputtered Nanocrystalline Ni₃Al coating*, in *Surface Engineering and Corrosion, Proc. Inter. Conf. on Surf. Sci. & Eng.*, R. Zhu, ed. (International Academic Publishers, Beijing, 1995), pp. 465.

14. F. Wang, H. Lou, and W. Wu, *Oxid. Met.* **43**, 395 (1995).
15. F. Wang and H. Lou, *Mater. Sci. Eng.* **A129**, 279 (1990).
16. F. Wang, H. Lou, and W. Wu, *Vacuum* **43**, 749 (1992).
17. F. Wang, H. Lou, S. Zhu, and W. Wu, *Oxid. Met.* **45**, 39 (1996).
18. F. Wang, *Oxid. Met.* (to be published).
19. F. Wang, H. Lou, S. Zhu, and W. Wu, *Corros. Sci. Prot. Technol.* **6**, 287 (1994) (in Chinese).
20. H. J. Klam, H. Hahn, and H. Gleiter, *Acta Metall.* **35**, 2102 (1978).
21. J. Karch, R. C. Briant, and H. Gleiter, *Nature* **330**, 556 (1987).
22. C. S. Tedmon, Jr., *J. Electrochem. Soc.* **114**, 788 (1967).