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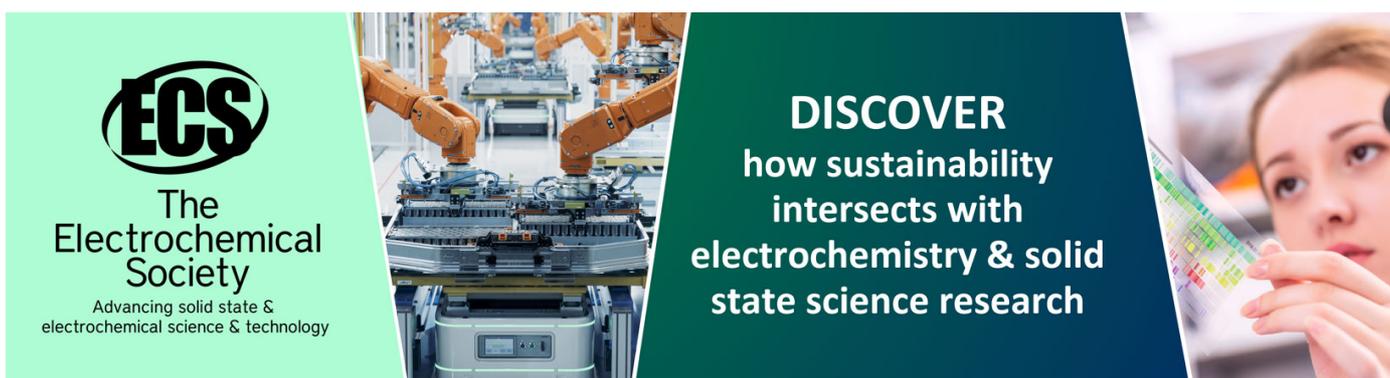
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High temperature oxidation of Ni-20Cr alloy under compressive stress

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Abstract. The effect of compressive stress on the oxidation kinetics and the revolution of the surface morphology formed on Ni-20Cr alloy was investigated at 900°C. The study was carried out mainly by comparisons of surface morphology of oxidized samples observed by scanning electronic microscopy. And the oxidation kinetics curves were assessed by two kinds of thermalgravimetric methods. The results indicate that applying the compressive stress induced an increase in the oxidation rate when the applied stress lowered 5MPa. Failure of the oxide scales is depended on the stress level, exceeding 5MPa the oxide scales began to crack and even spall.

1. Introduction

Ni-based superalloys are being used in gas turbines, aerospace, heating-treating industries and other high temperature fields due to their favourable strength and oxidation resistance at high temperatures [1, 2]. The strength is attributed to the formation of γ and γ' phases[3]. The oxidation resistance is related to the protective surface oxide scale of Cr- or Al-oxides [4, 5]. Under the above-mentioned applications, the superalloys undergo thermal cycling, high temperature and inevitably applied stress, which shortens the service lifetime of the superalloys. Then, the research on the oxidation of Ni-based superalloys under thermal cycling and applied stress is carried out. Thermal cycling of Ni-based superalloy has been extensively studied [6-8]. However, the effect of applied stress on the oxidation behaviour of Ni-based superalloys is much sparser. During the limited investigations, Barnard et al. studied the effect of applied tensile stress on the isothermal and cyclic oxidation behaviour of two superalloys, found that the applied stress promoted the faster formation of Cr_2O_3 layer [9]. Karabela et al. investigated the effect of cyclic stress on the oxidation damage of RR 1000 superalloy, indicated that the applied cyclic stress did not change the nature of oxidation damage but enhanced the extent of oxidation damage [10].

As the base of the Ni-based superalloy, Ni-Cr binary alloys are commonly used to explore the various properties. The oxidation behaviour of Ni-Cr alloys has been extensively studied. Most of them are concerned about the oxidation mechanism and the effect of the rare-earth element [11-13]. Few investigations deal with the effect of applied stress on the oxidation behaviour. Calvarin-Amiri et al. studied the effect of tensile stress on the oxide-layer microstructure and on the oxidation mechanism of Ni-20Cr foils, found that the applying stress induced an increase in the oxidation rate due to the formation of fast-diffusion by short-circuit paths [14, 15]. Zhou et al. investigated the oxidation behaviour of Ni-10Cr alloy under the compressive stress, indicated that the applied stress induced the prior formation of Cr_2O_3 and promoted the growth rate of oxide scales[16, 17]. In the present work, the authors studied the effect of compressive stress on the oxidation behaviour of Ni-



20Cr alloy. It was found that the growth behaviour of the oxide scale on Ni-20Cr alloy was related to the stress level.

2. Materials and experimental procedures

A nominal composition of Ni-20Cr alloy was melted by a consumable electrode vacuum furnace with electromagnetic stirring, then forged into rectangular ingots. The actual composition was Ni-23.08 Cr after confirming by energy dispersive X-ray spectroscopy (EDS). Samples with dimensions of 8mm×8mm×12mm and 2mm×8mm×12mm were cut for compressive and comparative tests. Prior to oxidation, the samples were abraded to 2000 grit (2.5µm) and ultrasonically cleaned in ethanol and then in acetone.

The oxidation kinetics curves were assessed by discontinuous methods. Two detailed measurements were carried out. (I) Many samples were used to plot one fully kinetics curve (Method I). (II) A sample was used to plot one fully kinetics curve (Method II). And all the samples were, firstly, weighed and measured and then exposed to the high temperature oxidation for a given time, removed, and reweighed. Finally, the oxidation kinetics curves were drawn based on the weight gain. After each test, all samples were observed and analysed on the surfaces by scanning electron microscopy (SEM) equipped with an EDS. Also, X-ray diffraction (XRD) was employed to analyse the composition of the oxide product.

3. Results and discussion

Figure 1 shows the weight gains, measured by two methods, of Ni-20Cr alloy with the increasing time after oxidation under the compressive stress. An obvious difference is displayed that the weight gain of method II was higher than that of the method I, which reveals the effect of the measurement method on the kinetics data. Nevertheless, a fact needs to ensure that the weight gains at measuring time under the compressive condition of two methods are both higher than that of the unstressed case, as shown in Figure 1(b). It should be noted that the oxide products formed on different kinds of Ni-20Cr alloy are different. According to the present investigations, an outer NiO layer, a media NiCr₂O₄ layer and an inner Cr₂O₃ are formed for Ni-20Cr alloys, although the Wagner theory points out the critical value for forming a protective oxide scale is near 20% Cr in weight. It is attributed to short-circuit diffusion paths in the alloy, such as voids, dislocations and grain boundaries, which affect the transient oxidation stage. Since the NiO grows much more rapidly than Cr₂O₃, a significant amount of NiO and NiCr₂O₄ can form before a continuous Cr₂O₃ layer can form [4]. It is also pointed out that higher contents of Cr, lower oxygen pressures, and cold-worked treatment can reduce the amount of Ni-rich oxide [4], conversely promote the nucleation and growth of Cr₂O₃. In the present work, oxide products formed under the two methods were different. Figure 2 shows the surface morphology to reveal different oxide product. Facet oxide in Figure 2(a) is a classic nature of NiO [18], and which was confirmed by EDS analysis. While particle oxide in Figure 2(b) is established as Cr₂O₃ after examining by EDS analysis. As the method II underwent the combined effect of compressive stress and thermal stress during the cooling and heating stage, the initial formation of Cr₂O₃ was prone to spall, and the left NiO covered the alloy surface and dominated the growth of oxide scale on the Ni-20Cr alloy. Once the Cr₂O₃ oxides continuous growth on the surface of the oxide scale, the growth rate was lower than that dominated by the growth of NiO.

Figure 3 displays the surface morphology of Ni-20Cr alloy after 72 h of oxidation when the samples were subjected to a serious of compressive stress. In the case of 5MPa, seen from Figure 3(a), many granular-grained oxides embodied in the underlying oxide layer were shown. Occasional nudes and obvious cracks were formed on the surface of the samples oxidized under 8MPa, as shown in Figure 3(b). Up to 10MPa, the number and amount of cracks were increased in comparison with that at 8MPa, and loose oxide morphology was displayed. Besides cracks in the oxide layer, in the 15MPa case, wedge-like oxide bands in the vicinity of the cracks were observed.

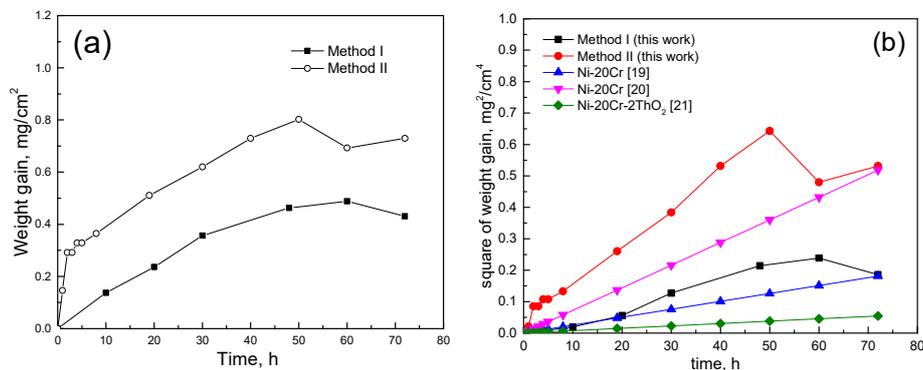


Figure 1. Oxidation kinetics curves for Ni-20Cr alloy oxidized under compressive stress (a) the relation between weight gain and time for two measuring methods; (b) the relation of square of weight gain and time (note: the linear fitting date was calculated by oxidation rate constant in the reference [19-21], i.e. $7.0 \times 10^{-7} \text{ mg}^2/\text{cm}^4 \cdot \text{s}$ [19], $2.0 \times 10^{-6} \text{ mg}^2/\text{cm}^4 \cdot \text{s}$ [20], $2.1 \times 10^{-7} \text{ mg}^2/\text{cm}^4 \cdot \text{s}$ [21])

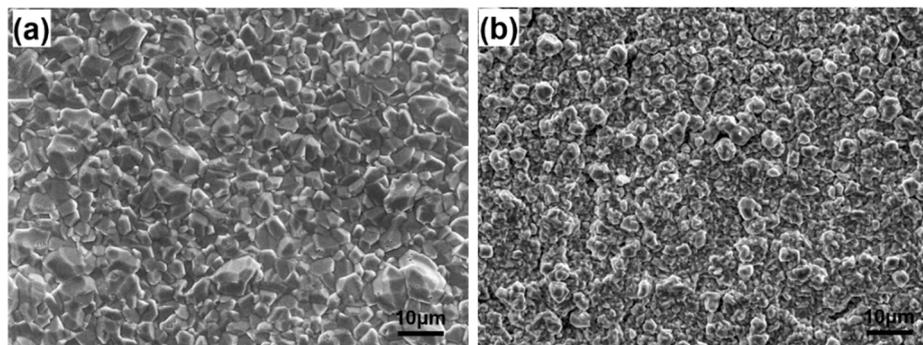


Figure 2. Surface morphologies of Ni-20Cr alloy oxidized under compressive stress (a) method II; (b) method I

To further examine the surface morphology feature in detail, high magnification SEM images of the samples oxidized under a serious of compressive stress for 72h were indicated, as shown in Figure 4. Figure 4(a) and Figure 4(b) show local spalled zone for the samples oxidized under 8MPa. As it can be seen in Figure 4(a), new oxide particles formed on the naked surface. Besides, the grain boundary of the alloy was obviously observed, which implies the spallation is prone to occur at the fast growth sites because of the short-circuit diffusion at the grain boundary. From the Figure 4(b), the footprints of spalled oxide particles were displayed. Meanwhile, the triple grain boundary of oxide was shown, which also implies the growth of the granular-like oxide particles is dominated by the short-circuit diffusion. Besides the spallation, cracking evolution under the compressive stress is necessary to be emphasized examined. Figure 4(c)-4(e) show the cracking feature of the samples oxidized under 10MPa, 15MPa, and 20MPa, respectively. It can be seen from Figure 4(c) that obvious cracks formed in the oxide layer, even some island-like oxide particles were separated by the cracks. With the compressive stress increasing to 15MPa, the width of cracks was decreased in comparison with that under 10MPa, the wedge-like crack was displayed. Up to 20MPa, the cracks still existed and some combined granular oxide particles were formed.

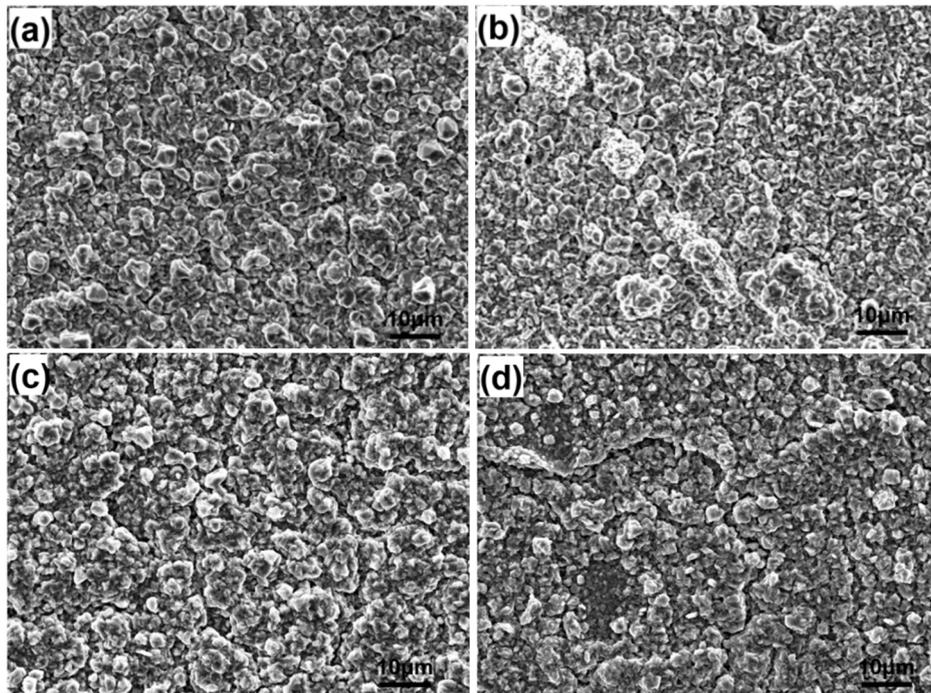


Figure 3. The surface morphologies of Ni-20Cr alloy after 72 h of oxidation under the applied compressive stress of (a) 5MPa; (b) 8MPa; (c) 10MPa; (d) 15MPa

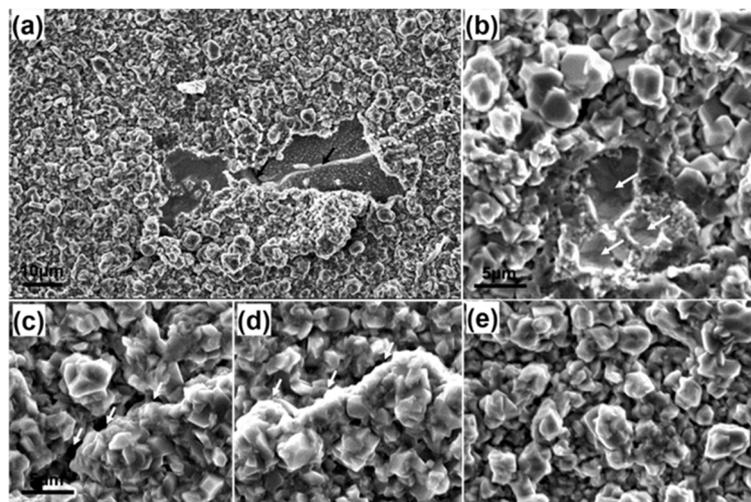


Figure 4. The high magnification surface morphologies of Ni-20Cr alloy after 72h of oxidation under a compressive stress of (a, b) 8MPa, (c) 10MPa; (d) 15MPa; (e) 20MPa

Based on the above mentions about the surface morphology evolution under the compressive stress, local spallation and cracking occurred. In order to further study the growth of the oxide scale under compressive conditions, the relation curve between the weight gain and compressive stress was drawn. Figure 5 shows the weight gains, measured by Method I, under different compressive stress after 72 h of oxidation. It is obvious that an increase in weight gain with the stress was exhibited when the applied stress was lower than 5 MPa. While exceeding 5 MPa, there is not significantly change in weight gain. As for the phenomenon, it is attributed to the effect of compressive stress on the growth and failure of the oxide scale. The increased growth of the oxide scale is commonly due to the fact that the applied stress can deduce more oxide nucleation sites at the initial oxidation stage [14-16, 22].

That enhanced oxide nucleation, accordingly made the oxide particles small, and more oxide grain boundaries are formed. During the continuous growth of the oxide scale, the short-circuit diffusion of grain boundary dominates the process, thereby increasing the growth of the oxide scale. Besides, the increased oxide nucleation also increases the weight gain to some extent. Therefore, the growth of the oxide scale is increased. The increased growth of oxide scale deduced by the applied stress is based on the intensity oxide layer. Once the oxide scale cracked and spalled, another affected mechanism on the growth of the oxide scale would be proposed. In another word, the unobvious effect of compressive stress on the growth of the oxide scale when the applied stress exceeded 5MPa should consider the oxide scale cracking and spallation.

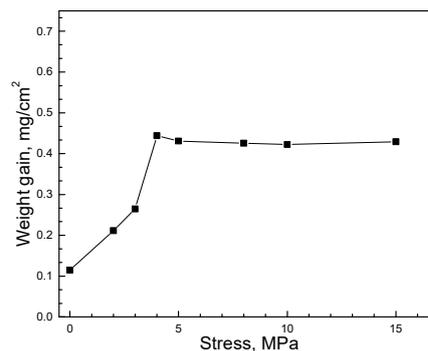


Figure 5. The relation between weight gain using Method I and applied stress after 72 h of oxidation

According to the surface morphologies in Figure 3 and Figure 4, the oxide scale cracked and spalled when the applied stress exceeds 5MPa. Meanwhile, new oxide would form at the spalled zone and in the vicinity of the cracks. In other words, the growth of the oxide scale under the compressive stress accompanied the weight gain and weight loss. Then, there would be a balance point between the weight gain and weight loss, resulting in that no net weight gain would continuously maintain. The change of weight gain after different dwells revealed the weight loss during the oxidation, which conversely explains the balance between weight loss and weight gain. Figure 6(a) displays the weight gain as functions with stress for the samples oxidized for 48h and 72h respectively. It can be seen that with increasing oxidation time, the weight more or less decreased no matter whether the samples were stressed or not. In the unstressed case, it is proposed that the growth stress because of the different volume between the oxide and the consumed metal during the oxidation is attributed to the spallation of the oxide scale. The applied compressive stress increased the stress in the oxide scale, which results in the spallation of the oxide scale more easily. With regard to the enhanced effect of compressive stress on the growth of the oxide scale, the overall weight gain under compressive stress is still higher than that in the unstressed case. However, the weight is decreased during the oxidation from 48h to 72h. The smaller the stress, the higher the change in weight between 48h and 72h of oxidation. It is indicated that the effect of compressive stress on the spallation is more obvious than on the growth of the oxide scale. Compared the surface morphologies of the samples after oxidizing for 48h and 72h in Figure 3, Figure 4 and Figure 6(b), Figure 6(c), it can be seen that there was no change in the surface morphologies formed on the samples at 48h and 72h under 5MPa stress. While, at 10MPa stress, the wedge-like oxide bands along the cracks formed at 48h of oxidation. Up to 72h, the wedge-like oxide band vanished, which exhibited that spallation occurred and left cracks, thus the weight somewhat decreased. When increasing the stress to 15MPa, the metal would deform in the compressive direction, which results in the close of the cracks, even wedge-like cracks generated again, as shown in Figure 4(d). Up to 20MPa, the metal underwent severe deformation, which deduced the wedge-like oxide band spall due to the buckling of the oxide scale in the vicinity of the wedge-like cracks, as shown in Figure 4(e).

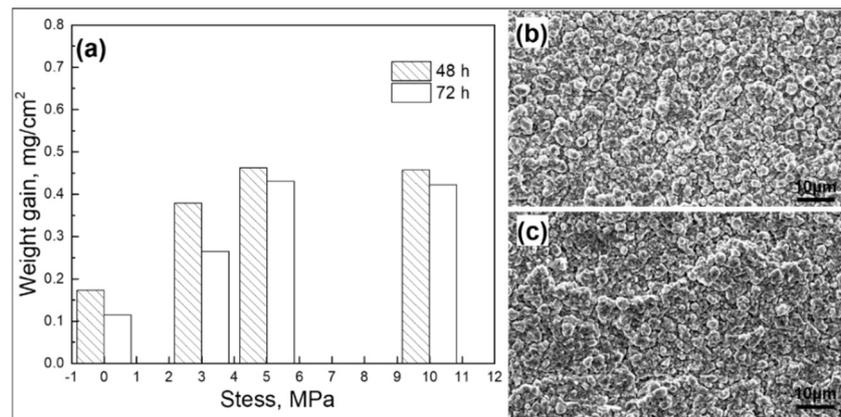


Figure 6. The relation between weight gain and stress (a) and the surface morphologies of Ni-20Cr oxidized under a compressive of (b) 5MPa; (c) 10MPa for 48h

Then, the effect of compressive stress on the oxidation behaviour of Ni-20Cr alloy is mainly related to the growth and failure of the oxide scale. The differences of oxidation under a serious applied stress are the following.

Under small compressive stress lower 5MPa, the oxide scale was intensity in spite of the formation of granular oxide particles. The growth of the oxide scale is increased by the applied stress, which has been extensively explained by the fact that the oxide nucleation would be enhanced by the applied stress. That effect indirectly deduced short-circuit diffusion in the form of grain boundary, which is prone to enhance the growth of oxide scale.

With the increasing compressive stress, cracking and spalling of the oxide scale is inevitable. Though the short-circuit diffusion paths, such as cracks and spallation zone, are increased, the overall weight gains are not certainly increased. It is the balance of weight gain and weight loss. Therefore, the growth kinetics of oxide scale is uncertain depended on the effect of compressive stress on the growth and the spallation of oxide scales. In the present work, the oxidation of Ni-20Cr alloy under compressive stress is limited to 20MPa. The growth of the oxide scale is increased by the applied stress when the stress lowers 5MPa, which is based on the intensity oxide scale. The failure of the oxide scale is not only due to the oxide scale mechanical properties but also the cooperative formation of both the oxide scale and metal. Therefore, the wedge-like cracks are generated. Up to 20MPa, wedge-like cracks vanished and net-like cracks formed, i.e. island-like oxide particles were separated by the cracks.

4. Conclusions

Weighting method for drawing the oxidation kinetics of Ni-20Cr alloy oxidized under compressive stress resulted in the significant difference in oxidation rate. Applying compressive stress induced the formation of uniform Cr_2O_3 scale (Method I). While undergoing thermal stress (Method II), the Cr_2O_3 scale was damaged, and NiO scale formed in the vicinity of the sample surface. Nevertheless, applying compressive stress induced an increase in the oxidation rate of Ni-20Cr alloy. The oxide scales on Ni-20Cr alloy began to crack and even spall only when the applied stress higher than 5MPa. The morphologies of cracks underwent a serious change from crack, wedge-like crack to the net-like crack.

Acknowledgments

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