Effect of further Alloying Elements on Corrosion Resistance of Ni-Cr Alloys in Molten Glass

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Abstract

The corrosion behaviour of commercial Ni-Cr alloys added with Fe, Ti, Nb and Al was evaluated in molten glass at 1050 °C. The static-immersion results reveal that the corrosion depth after testing for 100 h roughly remains at the same level for the alloys added with 5 wt.% Al or added with Fe, Ti and Nb (FeTiNb) separately, but decreases greatly by co-adding 5 wt.% Al with FeTiNb. However, a further increase of Al content to 15 wt. % in the co-added alloy degrades the corrosion resistance. The corrosion mechanism was discussed based on the analysis of the corrosion layer.

Keywords: A. Ni-based alloy; A. Glass; B. SEM; B. EPMA; B. XRD; C.

High-temperature corrosion

1. Introduction

In the glass processing industry, the corrosion issue resulting from the molten glass attack is a big challenge to the lifetime of metallic components directly in contact with the melts [1-4]. It is widely accepted that the alloys suitable for this corrosive environment should possess good resistance to oxidation and molten glass, as well as desirable mechanical strength at high temperatures [2, 5, 6]. Currently, high chromium Ni-based alloys are the most promising alloys, because they meet the basic requirement for properties [5, 7, 8].

Over the past few years, much attentions have been attracted to the corrosion issue of Ni-Cr alloys [1, 5, 7-11]. There have been some common perspectives about the formation of protective Cr_2O_3 and the effect of Cr content: A chromia layer develops on pure chromium at relatively low temperatures ($<1025\text{ }^\circ\text{C}$) [8], however, it can't form at higher temperatures ($>1050\text{ }^\circ\text{C}$) due to the transition from a passive state to an active state [8, 12]. A similar phenomenon was observed for high chromium alloys [7]. In order to provide sufficient protection for Ni-Cr superalloys, Rapin et al [1] proposed the method of pre-oxidation treatment or anodic protection to maintain the passive state in the case of Ni-30Cr immersed in NC3S at $1100\text{ }^\circ\text{C}$. In addition, Lizarazu [10] reported that the corrosion rate varies with the Cr content in Ni-Cr alloys. Alloys with low and high Cr-content have a corrosion rate more than a decade higher than that with intermediate Cr-content, which is related to the different reactions referred to the alloys with various Cr-content.

It is worth to notice that, in Ni-base alloys, many alloying elements except Ni and Cr are involved due to their specific contributions to the alloy performance. For example, Fe is an important constituent constructing the Ni-Fe base alloy [13]. Introducing iron improves the manufacturing facility remarkably and decreases the cost at the same time. As to some strengthening constituents such as Ti, Nb, and Al, they act as the γ' -phase formation element to enhance the high-temperature strength of alloys [14, 15]. The addition of above alloying elements is expected to exert a large influence on the corrosion behaviour of alloys in molten glass. Thus, it is critical to find out the role played by alloying elements in the molten-glass corrosion process at

high temperatures. It will also be benefiting from the understanding of this knowledge for designing candidate alloys with enhanced performances that can be used in extreme conditions in future applications. However, in current literature, there are few references on this related subject. The work of Horta [16] and Abdullaha [12] deals with the Fe-Al alloy and Ni-Cr-Al alloys, respectively. However, they have opposite views on the role of Al in alloy corrosion. The former concluded that protective alumina layer forms during corrosion, whereas the latter reported the failure of Al-containing alloys in molten salt. With regard to other additional elements, there is extremely limited information available.

The purpose of this study is to investigate the corrosion behaviour of candidate Ni-Cr alloys that possibly used in the molten-glass corrosive environment, thus to understand the influence of common alloying elements on the corrosion mechanism of alloys. In this paper, a series of **Ni-Cr** alloys with alloying elements, including Al, Ti, Nb, and Fe were designed and their corrosion resistance to molten glass was evaluated at 1050 °C. The alloys were statically immersed in molten glass for durations up to 100 h. The corrosion processes in the early and late stages of immersion were investigated through **scanning electron microscopy (SEM) and electron probe micro-analyzer (EPMA)** techniques. The corrosion mechanism for alloys with different compositions was revealed. The **effect of** additive elements **on the** corrosion process was also examined. The present work will provide useful information for designing alloys with high performances in the glass-processing application.

2. Materials and Experimental procedure

In this paper, five **Ni-Cr** alloys with Al, Fe, Ti, and Nb elements were designed and investigated based on the nominal compositions as shown in Table 1. Alloy 1 (A30) is a commercial Ni-Cr alloy, which has been widely used in the glass industry as a centrifugal spinner for fiberizing molten glass into fibers in rotary fiberizing processes. Based on the composition of A30, the other four alloys (Alloy 2 to Alloy 5) were designed with different elements, and named according to their compositions. For example, Alloy 4 (A30-5Al-FeTiNb) represents the alloy added with 5 wt. % Al and

combination addition of Fe, Ti and Nb (FeTiNb). The Al content ranging from 5-15 wt. % aims to improve the oxidation resistance at high temperature and to investigate the effect of Al on the corrosion rate in a large range. In previous work, the authors of this paper have found that the additional Ti and Nb in a proper content range enhance the high-temperature strength effectively. Therefore, in this study appropriate amount of these two elements were contained in the designed alloys. In addition, the effect of Fe element was also considered by adjusting Fe content from ~6 to 20 wt. % due to its superiority on the alloy processing and low cost. The cast ingots of these newly-developed **Ni-Cr** alloys were prepared via vacuum induction melting.

The samples for corrosion test were cut into a dimension of 8×10×2mm, ground to 600# SiC sandpaper and cleaned with ethanol ultrasonically. Each sample was placed in a 1 mm-thick alumina crucible full filled with soda-lime glass for the glass-fiber production (64.5%SiO₂–0.15%Fe₂O₃–3.40%Al₂O₃–0.1%SO₃–7.2%CaO–16.0%Na₂O–1.20%K₂O–4.5%B₂O₃ in wt.%). The immersion test was performed at 1050 °C for durations of 5 h and 100 h, respectively. When the temperature of furnace reached 1050 °C, the crucibles with **samples** and glass were put into the furnace. After the immersion test, the crucibles were taken out of the furnace and cooled in air. **Since most of the glass on sample surface has been peeled off during the cooling due to the high thermal stress, only a small amount of glass can be preserved and hence hardly observed in SEM images.**

The microstructure of the raw materials and samples after corrosion test were characterized by TEOL JSM-6060 type field emission scanning electron microscopy (FE-SEM). The samples were mounted with polymer before observation, followed by grinding and polishing. The phase structure of the alloys was determined by Rigaku RINT-TTR III X-ray diffraction (XRD). In addition, **EPMA** was utilized to analyse the elemental distribution of alloys.

3. Results and discussion

3.1 Characterization of cast alloys

Microstructures of cast alloys under the back-scattered electron mode are presented

in Fig.1, and their phase structures determined by XRD are shown in Fig. 2. Alloy 1 consists of γ -(Ni,Fe) matrix and chromium carbides along grain boundaries, the latter was identified to be Cr_{23}C_6 as seen in Fig. 2. Single addition of 5 wt. % Al (Alloy 2) or FeTiNb (Alloy 3), as well as introducing both of them (Alloy 4), maintains the same major matrix of γ -(Ni,Fe) as Alloy 1, except for a small amount of Al-rich phase observed in Alloy 4 (Fig. d). The addition of FeTiNb produces (Nb,Ti)-rich carbide with the brightest contrast, as indicated in Fig. 1c, d, and e, which has been detected in the XRD patterns in Fig. 2. Different from the above alloys, high Al content of 15 wt. % leads to a transition of phase structure from γ -(Ni,Fe) to a homogeneous mixture of dark Al-rich phase and light (Fe,Cr)-rich phase, with dispersed (Nb,Ti)C particles as well as some Cr_{23}C_6 in Alloy 5 (Fig. 1e).

The results of XRD pattern are consistent with the microstructure observed by SEM in Fig. 1. Alloys 1 to 4 has the same structure of γ -(Ni,Fe). No Al-rich phase was detected when Al content is at a low level (Alloys 2 and 4). Based on the above results, it can be inferred that, 5 wt. % Al does not change the major phase structure, and increasing Fe content from 6 to 20 wt. % has the similar effect, however, high Al content promotes the formation of NiAl phase.

3.2 Microstructures of alloys after molten glass corrosion

Figure 3 shows the SEM images in the back-scattered electron mode of alloys after glass corrosion at 1050 °C for 5 h and 100 h, respectively. The results at the initial stage of immersion give useful information about where corrosion begins. It is clear that, commercial Alloy 1 shows a typical characteristic of glass attack along the Cr-rich phase (dark), since the corrosion voids elongate in the direction where Cr_{23}C_6 precipitate, as indicated by the arrows in Fig. 3a. Similar to Alloy 1, Alloy 3 with FeTiNb exhibits the same corrosion feature preferentially along chromium carbides (Fig. 3e). Conversely, the corrosion voids seem to be dispersed more randomly on the surface of Alloy 3 with 5Al addition (Fig. 3c). By adding 5 wt. % Al and FeTiNb together, Alloy 4 forms a surface Nb-rich layer, with a thickness of $\sim 1\ \mu\text{m}$ after 5 h immersion (Fig. 3g), which is not present in other cases. In terms of high Al Alloy 5,

selective corrosion proceeds at the NiAl phase (Fig. 3i). Massive dissolution occurs to the NiAl constituent, leaving the skeleton of (Fe, Cr) phase.

After 100 h immersion, molten glass penetrates deeper into the base alloys, and there are no new features present except for the thickening of surface corrosion layer in comparison with the early stage. The alloy dissolution makes the surface layer porous to varying extents. It is notable that, Alloy 4 and Alloy 5 suffer from the least and the most corrosion attacks among all alloys, respectively, and the other three alloys are in a relatively medium level of corrosion. The Nb-rich layer is still present on the surface of Alloy 4, affording sufficient protection for the base alloy. In contrast, plenty of corrosion pores can be observed for Alloy 5, and the outermost layer of which has hardly adhesion with the subscale. In addition, the Cr-rich or Al-rich phases initially present on the near-surface layer have disappeared after 100 h in all cases.

The average corrosion depth of alloys after immersion for 100 h was measured using SEM images, taken from 6 different regions for each sample, and the averages along with standard deviations are shown in Table 2. The commercial Alloy 1 corrodes for ~ 75.7 μm thick after 100 h, and Alloy 2 with 5Al and Alloy 3 with FeTiNb yield the values of ~ 70.8 μm and 71.0 μm , respectively, roughly at the same level with Alloy 1. Alloy 4 possesses superior corrosion resistance because of the smallest corrosion depth of ~ 17.8 μm , as a contrast, the value for Alloy 5 is as high as ~ 81.3 μm .

Based on the above results, it is clear that the individual addition of 5 wt. % Al, or FeTiNb does not degrade the corrosion behaviour of Alloy 1. However, rather surprisingly, when combining the above additions to form Alloy 4, it has an excellent positive effect on improving the resistance to glass attack with the formation of Nb-rich layer. Nevertheless, a further increase of Al content up to 15 wt. % is apparently favouring the corrosion of NiAl phase with a negative effect on the corrosion resistance.

3.3 Characterization of the phase structure and element distribution

Figure 4 shows the XRD patterns of alloys after corrosion for 100 h in molten glass

at 1050 °C. Alloy 1 to 3 shows the same phase structure of γ -(Ni,Fe) as the cast alloys in Fig. 2, indicating no protective product develops for these three alloys, which is consistent with the microstructure observed in Fig. 3. The disappearance of carbides peaks is due to the dissolution of Cr-carbide on the surface layer. $\text{Nb}_6\text{Ni}_{16}\text{Si}_7$ is detected on Alloy 4, which corresponds to the Nb-rich phase observed in Fig. 3g and 3h. $\text{Cr}_{6.5}\text{Ni}_{2.5}\text{Si}$ forms on Alloy 5 with high Al content. Since there is no silicon in Alloys 4 and 5, the Si-containing compound is believed to be resulting from the reduction of SiO_2 in glass [1, 17].

In order to further explore the corrosion process during immersion, EPMA mapping of cross sections of alloys was conducted, and the elemental distribution is shown in Figures 5 to 9. Figure 5 gives the mapping result of Alloy 1 (A30), it can be seen that the aggressive molten glass tends to attack Cr-rich constituent first because the corrosion voids caused by dissolution are along the locations where carbides precipitated. Furthermore, significant Cr-depletion layer of $\sim 75\ \mu\text{m}$ thick is also observed in Fig. 5b, whereas such an impoverishment is not observed for the other constituents. Within the same region where Cr is depleted, silicon is found to be concentrated as seen from the Si profile in Fig. 5e, which comes from the glass by the reduction reaction [12]. Thus, the damage of Alloys 1 is driven primarily by the selective dissolution of Cr.

The EPMA mapping results of Alloy 2 with 5Al addition are displayed in Fig. 6. Al profile in Fig. 6b reveals an Al-depletion layer with a thickness of $\sim 95\ \mu\text{m}$, while the value of the Cr-depletion layer is only $\sim 63\ \mu\text{m}$ (Fig. 6c), owing to the much lower Al content (5 wt. %) than Cr (26 wt. %) in the original alloy. This result indicates both Al and Cr participate in the corrosion process. It needs to be noticed that the shapes and distribution of corrosion voids are no longer in accordance with the Cr-rich phase in the far field alloy, that is, they are prone to distribute more uniformly compared with previous Alloy 1. Moreover, by adding 5 wt. % Al into Alloy 1, the Cr depletion on surface layer has been weakened (Fig. 6c), which can be distinguished from the thickness and the steepness of colour change within the Cr-depleted layer compared with that in Fig. 5b. Therefore, it is reasonable to infer that the corrosion of Cr is

limited by Al dissolution to some extent.

Figure 7 presents the mapping results of Alloy 3 with alloyed FeTiNb. Cr is found to be critically depleted in corrosion layer along the chromium carbides (Fig. 7b), the same as Alloy 1. Although 20 wt. % Fe was introduced to this alloy, no evidence of massive corrosion to Fe element is observed (Fig. 7c), which is possibly related to the higher stability of Fe than Cr in molten glass as indicated in previous work [8]. Nb and Ti are observed to be slightly depleted near the surface layer as seen in Fig. 7g and Fig. 7h. Comparing the profiles of Nb (Fig. 7h) and Cr (Fig. 7b), it can be inferred that Cr-rich carbide is more likely to be corroded than Nb, due to the thinner depletion layer of Nb. On basis of the results in Fig. 5 and 7, the addition of FeTiNb in Alloy 1 has no significant effect on the element distribution during the corrosion, and both Alloy 1 and Alloy 3 exhibit the typical Cr-dissolution induced alloy failure.

The results of Alloy 4 with combined FeTiNb and 5Al addition are given in Fig. 8. The thickness of the Al-depletion layer is $\sim 75\text{ }\mu\text{m}$ (Fig. 8b), much thinner than that of Alloy 2 with 5Al. Meanwhile, the Cr seems to be immune from the glass corrosion (Fig. 8c). Although the dissolution of Cr-rich phase still occurs, the areas not containing Cr-rich precipitates exhibit the same colour intensity as that in base alloy. Moreover, a layer rich in Nb, Ni, and Si is observed at the interface of alloy/glass (Fig. 8e, h and i). This is completely in accordance with the microstructure and XRD results in Fig. 3 and Fig. 4. The contrast between the corrosion behaviour of Alloy 2 and Alloy 4 is probably owing to the formation of this $\text{Nb}_6\text{Ni}_{16}\text{Si}$ layer. In the case of Alloy 4, the dissolution of active Al and Cr are both inhibited, which is proved by the results in Fig. 8b and c.

The mapping results of Alloy 5 with 15Al and FeTiNb are shown in Fig. 9. It can be observed that corrosion occurs in a totally different way with respect to Alloy 1 to 4: the surface of Alloy 5 dissolves severely, producing a rather loose corrosion layer of $\sim 79\text{ }\mu\text{m}$ with substantial pores. No $\text{Nb}_6\text{Ni}_{16}\text{Si}_7$ layer is present, which is in agreement with the XRD results in Fig. 4. Since the NiAl phase is confirmed to be dissolved first in Section 3.1, the depletion for Al and Ni is both observed in mapping results (Fig. 9b and Fig. 9e). Another distinct feature is that there is hardly

impoverishment in Cr profile (Fig. 10c), instead, the surface is rich in chromium. This indicates that the corrosion of Alloy 5 is predominated by the dissolution of Al-rich phase. In turn, Cr is almost restrained from corrosion.

In addition to Al and Cr, Ti is another active element at high temperatures. In this study, the alloys with 0.5 wt.% Ti (Alloy 3, 4 and 5) exhibit a slight Ti depletion to various extents, which can be observed from the Ti profiles of EPMA as shown in Fig. 7g, 8g and 9g, suggesting that Ti has relatively high activity and is expected to dissolve in glass like Al and Cr. Except for such a trend of active dissolution, there is no evidence of the interaction between Ti and Nb₆Ni₁₆Si₇ surface layer, or other distinct corrosion characteristics. Therefore, Ti seems not to change the corrosion mechanism. In view of the low level of Ti content in this study, the role of Ti in the corrosion process can be negligible in the composition range of 0-0.5 wt. %. However, if the content of Ti in the alloy increases to some critical value, the impact of Ti should also be considered.

3.4 Corrosion mechanism

Based on the above results, the alloying elements of Fe, Al, Ti, and Nb have individually variable, or even interaction effect on the corrosion behaviour of Ni-Cr alloys. The corrosion mechanism can be illustrated schematically in Fig. 10. The first mechanism for alloys without Al addition is presented in Fig. 10a. Corrosion begins at the locations where Cr-rich carbides precipitate at the early stage of corrosion. In the late stage, further penetration of molten glass occurs along the pores produced by the dissolution of chromium carbides. The reactions at the alloy/glass interface are the oxidation of Cr and the reduction of SiO₂ from the network in glass, which can be written as the following equations [18-20]:

From the above results, it can be inferred that both Alloy 1 and 3 follow this corrosion process. Therefore, the FeTiNb has no apparent influence on the corrosion mechanism.

The second mechanism aims to explain the corrosion of alloys with the minor Al content as seen in Fig. 10b. For Alloy 2 with 5 wt. % Al, aluminium participates in the corrosion together with chromium. According to our previous work on Ni-base alloys with Al addition, Al is more likely to dissolve in molten glass due to its higher chemical activity than Cr, which has also been proved by other investigations [12, 21]. As a consequence, the existence of Al in alloys makes itself corroded preferentially, furthermore, the attack aiming at chromium is inhibited to some extent. Thus, the corrosion tends to proceed uniformly in Alloy 2. In this case, the corrosion reactions are the oxidation of both Al (Eq. 3) and Cr, together with the reduction of SiO_2 . Even though the corrosion of Al proceeds much faster than that of Cr, the corrosion rate obtained by corrosion depth still maintains at the same level with Alloy 1 without Al (Fig. 3). This is because the corrosion in this case is controlled by the diffusion of Al from the base alloy to the interface, due to the limited Al content. For this reason, the minor Al addition is helpful to improve the corrosion resistance of Ni-Cr alloy, which has been reported in previous work.

Figure 10c explains the corrosion process of Alloy 4 with 5Al and FeTiNb, a protective layer of $\text{Nb}_6\text{Ni}_{16}\text{Si}_7$ starts to form on the alloy surface at initial stage of corrosion, the presence of which inhibits the diffusion of reactant and product species across the reaction interface. As a result, the corrosion of Al and Cr is significantly mitigated. Since it is not entirely continuous, slight corrosion still takes place in the underlying alloy, however, with a much thinner corrosion layer. Theoretically, the dissolution of $\text{Nb}_6\text{Ni}_{16}\text{Si}_7$ occurs spontaneously along with its formation in molten glass at high temperature, and the durability of this film depends on the competition between these two processes. After 100 h immersion, the $\text{Nb}_6\text{Ni}_{16}\text{Si}_7$ layer is still protective for Alloy 4, indicating that the solubility of $\text{Nb}_6\text{Ni}_{16}\text{Si}_7$ in glass is relatively small and the formation prevails in the dissolution process over 100 h duration.

Figure 10d illustrates the corrosion of high Al alloy. When the Al content increases to 15 wt. %, the NiAl phase undergoes selective corrosion in molten glass. Along with the massive dissolution of Al-rich phase, the surface layer becomes loose, porous and discrete, losing the diffusion paths for Nb access to the surface. Therefore, Nb-rich

phase is dispersed in **the** alloy, instead of enriching on the surface. In addition, the dissolution of Al proceeds according to the interface reaction of Eq. 3 without diffusion-controlled process, due to the sufficient Al content (15 wt. %) supplied by high Al substrate, which is proved by the absence of surface Al-depletion layer. As a result, Alloy 5 corrodes **rapidly** with the highest corrosion depth as **shown** in **Table 2**. Meanwhile, the corrosion of chromium element is almost retarded due to its relatively low activity with respect to Al.

It is clear that the $\text{Nb}_6\text{Ni}_{16}\text{Si}_7$ layer is important to protect the alloy from the molten-glass dissolution process and **this** layer only forms when a small amount of Al is introduced **to Nb-added** alloys. The possible explanation for this phenomenon is that the addition of Al changes the dissolution mode of Ni-Cr alloys from a chromium-preferring one to **a** relatively uniform one, leading to the **increase in diffusion paths for Nb** to the surface. As is known that, grain boundaries provide the short diffusion paths of elements due to the high energy **at these locations** [22, 23]. From the mapping results of Alloy 3 in Fig. 7, it can be observed that NbC enriches mainly at the grain boundaries together with Cr carbides. When the glass penetrates inward and dissolves the Cr-rich carbides at grain boundaries, the outer-diffusion paths of Nb are destroyed. For this reason, Nb enrichment is not observed on Alloy 3. By adding Al into Ni-Cr alloy, the attack to Cr-rich carbides transfers to Al element and the corrosion no longer takes place merely along the grain boundaries. As a result, these diffusion routes are partially preserved and Nb has access to concentrate on the surface. This hypothesis is supported by the apparent evidence of corrosion voids along Cr-rich carbides for Alloy 1 and 3 (no Al addition), which becomes less distinct in the case of Alloy 2 and 4 containing minor Al. However, the knowledge of the durability and the factors that promote $\text{Nb}_6\text{Ni}_{16}\text{Si}_7$ generation still needs further investigations, which would be focused in our future work.

4. Conclusions

In this study, the corrosion behaviour of a commercial Ni-Cr alloy with different

alloying elements in molten glass at 1050 °C was investigated. Results indicate that:

1. The molten glass mainly attacks the Cr-rich carbide along grain boundaries in commercial Ni-Cr alloy;
2. The addition of FeTiNb has little influence on the corrosion behaviour of alloy;
3. Individual addition of 5wt. % Al results in the dissolution of both Al and Cr, changing the corrosion mode from a selective corrosion along chromium carbides to a uniform corrosion;
4. The alloy with co-added 5 wt. % Al and FeTiNb has the highest corrosion resistance among investigated alloys due to the formation of a protective $\text{Nb}_6\text{Ni}_{16}\text{Si}_7$ layer;
5. Excessive Al content of 15 wt. % has a detrimental effect on the corrosion resistance.

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Figure captions and Tables:

Fig. 1 Microstructures of the cast alloys: (a) Alloy 1 (A30), (b) Alloy 2 (A30-5Al), (c) Alloy 3 (A0-FeTiNb), (d) Alloy 4 (A30-5Al-FeTiNb), (e) Alloy 5 (A30-15Al-FeTiNb)

Fig. 2 XRD patterns of the cast alloys

Fig. 3 Cross section (SEM-BEI) of alloys after immersion in molten glass at 1050 °C for 5 h and 100 h: (a,b) Alloy 1, (c,d) Alloy 2, (e,f) Alloy 3, (g,h) Alloy 4, (i, j) Alloy 5

Fig. 4 XRD patterns of alloys after molten glass corrosion at 1050 °C for 100 h

Fig. 5 EPMA mapping results of Alloy 1 after molten glass corrosion at 1050 °C for 100 h

Fig. 6 EPMA mapping results of Alloy 2 after molten glass corrosion at 1050 °C for 100 h

Fig. 7 EPMA mapping results of Alloy 3 after molten glass corrosion at 1050 °C for 100 h

Fig. 8 EPMA mapping results of Alloy 4 after molten glass corrosion at 1050 °C for 100 h

Fig. 9 EPMA mapping results of Alloy 5 after molten glass corrosion at 1050 °C for 100 h

Fig. 10 Schematic diagrams of corrosion mechanism for Ni-Cr alloys: (a) without Al; (b) with low levels of Al (5 wt.%); (c) with 5 wt.% Al and FeTiNb; (d) with 15 wt.% Al and FeTiNb

Table 1 The composition of alloys in mass percentage

Alloy	Composition (wt. %)						
	Cr	Al	Fe	Ti	Nb	Others	Ni
1 (A30)	28	—	6.0	—	—	C:0.7, Si:0.6 W:7.4	Bal.
2 (A30-5Al)	26	5	5.7	—	—	C:0.66 W:7.03	Bal.
3 (A30-FeTiNb)	25	—	20	0.5	1.5	C:0.69 W:7.25	Bal.
4 (A30-5Al-FeTiNb)	25	5	20	0.5	2.0	C:0.64 W:6.81	Bal.
5 (A30-15Al-FeTiNb)	25	15	20	0.5	2.0	C:0.63 W:6.66	Bal.

Table 2 The average corrosion depth of alloys after corrosion in molten glass at 1050 °C for 100 h

Alloy No.	1	2	3	4	5
Corrosion depth (μm) $\pm$ SD* (μm)	75.7 $\pm$ 6.6	70.8 $\pm$ 6.0	71.0 $\pm$ 5.5	17.8 $\pm$ 1.5	81.3 $\pm$ 4.8

*SD refers to the standard deviation of values extracted from different areas.

Fig. 1 Microstructures of the cast alloys: (a) Alloy 1 (A30), (b) Alloy 2 (A30-5Al), (c) Alloy 3(A30-FeTiNb), (d) Alloy 4 (A30-5Al-FeTiNb), (e) Alloy 5 (A30-15Al-FeTiNb)

Fig. 2 XRD patterns of the cast alloys

Fig.3 Microstructures of alloys after immersion in molten glass at 1050 °C for 5 h and 100 h: (a,b) Alloy 1, (c,d) Alloy 2, (e,f) Alloy 3, (g,h) Alloy 4, (i, j) Alloy 5

Fig. 4 XRD patterns of alloys after molten glass corrosion at 1050 °C for 100 h

Fig. 5 EPMA mapping results of Alloy 1 after molten glass corrosion at 1050 °C for 100 h

Fig. 6 EPMA mapping results of Alloy 2 after molten glass corrosion at 1050 °C for 100 h

Fig. 7 EPMA mapping results of Alloy 3 after molten glass corrosion at 1050 °C for 100 h

Fig. 8 EPMA mapping results of Alloy 4 after molten glass corrosion at 1050 °C for 100 h

Fig. 9 EPMA mapping results of Alloy 5 after molten glass corrosion at 1050 °C for 100 h

Fig. 10 Schematic diagrams of corrosion mechanism for Ni-Cr alloys: (a) without Al; (b) with low levels of Al (5 wt.%); (c) with 5 wt.% Al and FeTiNb; (d) with 15 wt.% Al and FeTiNb