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Pitting resistance evaluation of ternary Ni-Cr-Mo alloys in flue gas environment

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ABSTRACT

After the appearance of pitting corrosion, the corrosion rate reaches very high values, which leads to a deterioration in the quality of the product in a short time. It may happen that the pitting does not continue its penetrating effect: if there are no necessary conditions for its growth, a pitting of greater activity is not formed, which will absorb all the current supplied from the area surrounding the cathode. Results of potentiodynamic investigations of four Ni-base alloys are presented. The tests were conducted in 1 percent sulphuric acid, containing 0.2 percent chlorides at temperature 353K. Gravimetric test, performed in the same conditions, revealed excellent properties of alloy signed A3. Pitting corrosion of alloy A4 at the test conditions after long exposure at 353K was observed and was confirmed by the applied tests. The multiple anodic polarization (MAP) method is proposed to control alloys' susceptibility to pitting corrosion.

Keywords: pitting, alloy, anodic polarization.

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Introduction

High performance nickel alloys have been applied during the years at critical zones of flue gas desulphurization (FGD) units. Among them alloys A1 and A2 have a number years of proven service, alloy A3 is the newest one with superior corrosion resistance and nitrogen enhanced alloy A4 presents. acidic corrosion resistance with reduced cost [1-3]. The composition of the alloys is shown in table 1.

Table 1 - Composition of investigated alloys

	Ni	Cr	Mo	W	Si	C	Fe
(A1)	57,5	15,85	16,15	3,6	0,05	0,004	5,70
(A2)	66,6	15,75	15,70	-	0,04	0,003	1,10
(A3)	59,0	22,50	15,90	-	0,02	0,002	0,23
(A4)	31,0	26,60	6,30	-	0,04	0,008	bal

There has been short experience with alloy A3 FGD applications mainly in the USA but not much has been reported on alloy A4. Nickel super alloys have been used for lime / limestone FGD systems not only for scrubbers but also at critical locations with more aggressive environments, such as out let ducts, repeaters, stacks and dampers Failure of an alloy occurs usually due to pitting corrosion, but also general corrosion, crevice corrosion, erosion n- corrosion or stress corrosion cracking may be involved.

Lately there has been some doubt emphasized on the differences of alloys properties when laboratory tests and field FGD practice has been considered. It was also stated that in diluted sulfuric-hydrochloric acid mixtures the resistance of alloys depends on the ratio of both acids. The high Mo alloy A1 has been announced to be usually superior to alloy C-22 in such an environment [4-7].

Experimental part

The alloy samples were supplied by one of the world best producer of Ni-base alloys and used in delivery condition for tests. They had plate shapes. At least 2 samples having dimensions 35 x 100 mm were used for corrosion tests. The exposure was carried out in 1 % H₂SO₄ (pH 1) solution at 353±2K. The test solution and the elevated exposure temperature simulated corrosion conditions of absorber upper zones, outlet ducts, reheat mixing zones and stacks in FGD plants. The solution formula was chosen from a number of electrolytes used for laboratory experiments simulating chosen FGD conditions. The polarizations were carried out using GAMRY INSTRUMENTS card for DC electrochemical measurements. Passive properties of alloys were checked by means of potentiokinetic standard anodic polarization (SAP). Resistance of alloys against pitting corrosion was investigated by means of cyclic polarization (CP) and five anodic polarizations finished with return polarization (MAP). Fifteen minutes break was used after each single anodic polarization within MAP had been finished. Each anodic polarization started from the corrosion potential. The potential scan rate was 10 mV/60s. A saturated calomel electrode was used as a reference.

The anodic polarization was performed from the corrosion potential until the current density achieved a value of about 1 mA/cm² for CP at that point the polarization direction was reversed. A reversed polarization was finished when the current density was close to the zero value. The weight loss

was determined after corrosion exposure carried out in glass vessels with air coolers situated in a sand bath. A scale on alloy A4 was removed by boiling in an alkaline solution with zinc dust. A weight change checked with unexposed sample showed no necessity for corrections. Pitting corrosion photographs of alloy A4 were taken using an optical microscope [8-10].

Results and discussion

From the SAP carried out at 353 K (figure 1, a-d) one can deduce that both A1 and A2 alloys behaviour was similar at these conditions and their passive state current was higher compared to alloy A3. At the end of the return polarization the potential of alloy A3 and alloy A4 was much more noble than the corrosion potential and this must be connected with the character of passive films. Such phenomena were not registered in the case of A1 and A2 alloys [11-13].

After MAP a high corrosion current was registered for alloy A4. Nearly no change of alloy A1 cyclic polarization curves was found after MAP (Fig.2 A, B). Circular small pits in the case of alloy A4 were observed after the test. The breakdown of the passive film occurs during the dynamic process of its growing. The pit formation depends probably on different phases in the alloy, like on the composition and morphology of the passive film. No pit was displayed when the alloy A4 sample was kept in the, transpassive state for the time equivalent to the MAP test period.

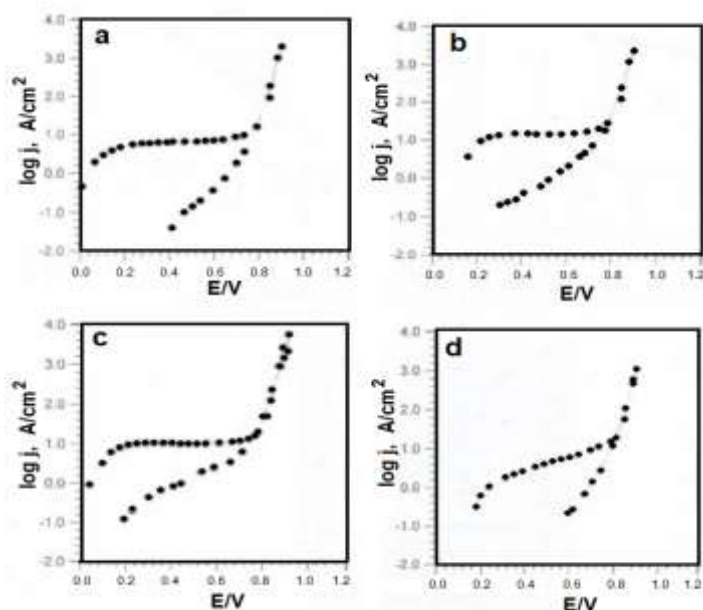


Figure 1 - Potentiokinetic anodic polarization of Ni-alloys: a - A1, b - A2, c - A3, d - A4

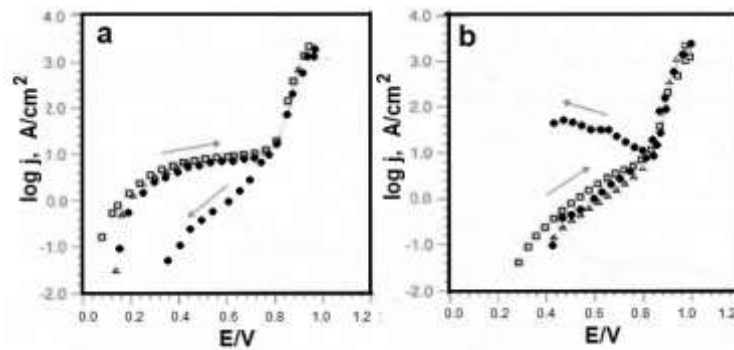


Figure 2 - Multiple potentiokinetic polarization (MAP) of Ni-alloys: a - A1, b - A4

Gravimetric test results after an exposure at 298 K gives an impression about good performance of alloy A4 in comparison with others. This has been confirmed after 21 days of exposure at 353 K because alloy A4 seems to be better than A1 and A2 alloys.

Nevertheless, when a yellow deposit was removed from the alloy A4 sample after 280 days of exposure the lowest durability of that alloy was demonstrated. Alloy A3 is least sensitive to the acidic solution in all gravimetric tests.

Alloy A1 is less susceptible to dissolution than alloy A2. The passive layer durability was controlled during long term corrosion exposure in the test solution at 353 K. No pitting corrosion was observed for high Mo alloys (A1, A2, A3) due to their high pitting resistance equivalent.

Pitting corrosion was observed with the naked eye on the surface of alloy A4 after 280 days of exposure [14-15]. It is obvious that the nitrogen content is not high enough to balance lower concentration of molybdenum in this alloy. The passive layer formed is not resistant enough to the environment, possibly due to passive film composition or defects.

The problem has to be studied more for an explanation. Mainly small diameter pits at the alloy surface could be seen, sometimes with caverns under the passive layer.

Conclusions

The alloy 59 proved its best corrosion resistance compared to C-276, C4 and 31 alloys in 1% sulfuric-hydrochloric (0,2%Cl-) acid solution simulating a chosen FGD environment at 353 K.

In such an environment pitting corrosion of alloy 31 occurs after a quite long incubation time. Alloy 31 demonstrates a high tendency to passivation in the test environment forming a protective layer with high dielectric properties. Nevertheless, the passive film cannot survive for a long time without a breakdown in the test conditions. The multiple potentiokinetic anodic polarization finished with cyclic polarization (MAP) can be applied to find the sensitivity of an alloy to pitting corrosion. There are limitations when short tests like cyclic polarization are applied to predict pitting corrosion of high performance nickel alloys.

Conflict of interests. On behalf of all authors, the correspondent author declares that there is no conflict of interests.

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Түтін газдарында Ni-Cr-Mo үштік қорытпалардың нүктелік коррозияға төзімділігін бағалау

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ТҮЙІНДЕМЕ

Нүктелік коррозия пайда болғаннан кейін коррозия өте жылдам жүреді, бұл өнім сапасының қысқа мерзімде нашарлауына әкеледі. Питтинг өзінің ену әрекетін келесі жағдайларда жалғастырмауы мүмкін: оның өсуіне қажетті жағдайлар болмағанда катодта қоршаған аймақтан келетін барлық тоқты сіңіретін үлкен белсенділік пайда болмайды. Жұмыста Ni негізіндегі төрт қорытпаның потенциодинамикалық зерттеулерінің нәтижелері келтірілген. Сынақтар 0,2% хлоридтен тұратын 1% күкірт қышқылында 353К температурада жүргізілді. Сол жағдайларда жүргізілген гравиметриялық сынақтар А3 қорытпасының өте жақсы қасиеттерін көрсетті. 353К-де ұзақ жүргізілген сынақтарда А4 қорытпасының нүктелік коррозиясы байқалды және қолданылған сынақтармен расталды. Қорытпалардың нүктелік коррозияға сезімталдығын бақылау үшін көп анодты поляризация (MAP) әдісі ұсынылды.

Түйін сөздер: қорытпа, питтинг, анодты поляризация.

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Оценка устойчивости к питтингу тройных сплавов Ni-Cr-Mo в среде ДЫМОВЫХ ГАЗОВ

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АННОТАЦИЯ

После появления точечной коррозии скорость коррозии достигает очень высоких значений, что в короткие сроки приводит к ухудшению качества изделия. Может случиться так, что питтинг не продолжит свое проникающее действие: если нет необходимых условий для его роста, не образуется питтинг большей активности, который поглотит весь ток, подаваемый из области, окружающей катод. Представлены результаты потенциодинамических исследований четырех сплавов на основе Ni. Испытания проводились в 1-процентной серной кислоте, содержащей 0,2 процента хлоридов, при температуре 353 К. Гравиметрические испытания, проведенные в тех же условиях, показали отличные свойства сплава, подписанного А3. Наблюдалась точечная коррозия сплава А4 в условиях испытаний после длительной выдержки при 353 К и была подтверждена примененными испытаниями. Предложен метод множественной анодной поляризации (MAP) для контроля восприимчивости сплавов к точечной коррозии.

Ключевые слова: питтинг, сплав, анодная поляризация.

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Reference

- [1] Mukashev, D., Muradov, A., Shiderova, R. Corrosion resistance of chrome-silox-carbon nano-composition electrolytic coatings. *International Multidisciplinary Scientific GeoConference Surveying Geology and Mining Ecology Management, SGEM*, 2016, 2016, pp. 71–77.
- [2] Ved', M., Sakhnenko, N., Yermolenko, I. et al. Composition and corrosion behavior of iron-cobalt-tungsten. *Eurasian Chemico-Technological Journal*, 2018, 20(2), pp. 145–152.
- [3] Belyaev, D.V., Mussabek, G., Sagyndykov, A. et al. Modern state of composite coatings formation problem. *International Multidisciplinary Scientific GeoConference Surveying Geology and Mining Ecology Management, SGEM*, 2017, 17(61), pp. 233–240.
- [4] Yar-Mukhamedova, G.Sh. Investigation of corrosion resistance of metallic composite thin-film systems before and after thermal treatment by the corrodokote method. *Materials Science*, 2001, 37(1), pp. 140–143.
- [5] Ved, M., Sakhnenko, N., Koziar, M. et al. Ternary cobalt-molybdenum-zirconium coatings for alternative energies. *Applied Surface Science*, 2017, 421, pp. 68–76.
- [6] Kemelzhanova A., Mukasev K., Yar-Mukhamedova G., Lampke Th. Investigation of the anticorrosion properties of nano-CEC in amine environments. *Kompleksnoe Ispol'zovanie Mineral'nogo syr'â = Complex Use of Mineral Resources*. 2020. Volume 2, Issue 313, pp.52-57. <https://doi.org/10.31643/2020/6445.17>
- [7] Yar-Mukhamedova, G.S. A mathematical model of formation of the structure of composite films by the cut-off method. *Materials Science*, 2000, 36(4), pp. 598–601.
- [8] Yar-Mukhamedova, G.Sh. Internal adsorption of admixtures in precipitates of metals. *Materials Science*, 1999, 35(4), pp. 598–600.
- [9] Sagyndykov, A.B., Kalkozova, Z.K., Yar-Mukhamedova, G.S., Abdullin, K.A. Fabrication of nanostructured silicon surface using selective chemical etching. *Technical Physics*, 2017, 62.
- [10] Muradov, A., Mukashev, K., Ismailova, G. et al. Mathematical model of composite materials formation. *International Multidisciplinary Scientific GeoConference Surveying Geology and Mining Ecology Management, SGEM*, 2017, 17(61), pp. 201–208.
- [11] Aldabergenova, T.M., Kislitsin, S.B., Larionov, A.S., Effect of low-energy alpha-particles irradiation on surface structure and physical-mechanical properties of high-purity tungsten. *AIP Conference Proceedings*, 2016, 1783, 020003.
- [12] Ved' M., Yermolenko I., Karakurkchi, A., Kemelzhanova, A. Effect of electrodeposition parameters on the composition and surface topography of nanostructured coatings by tungsten with iron and cobalt. *Eurasian Chemico-Technological Journal*, 2020, 22(1), pp. 19–25.
- [13] Yar-Mukhamedova, G.S., Darisheva, A.M., Yar-Mukhamedov, E.S. Adsorption of the Components of a Chrome-Plating Electrolyte on Dispersed Corundum Particles. *Materials Science*, 2019, 54(6), pp. 907–912.
- [14] Ved, M., Karakurkchi, A., Sakhnenko, N., Atchibayev, R. Research on the improvement of mixed titania and Co(Mn) oxide nano-composite coatings. *IOP Conference Series: Materials Science and Engineering*, 2018, 369(1), 012019.
- [15] Ved', M.V., Sakhnenko, N.D., Nenastina, T., Volobuyev, M. Ann simulation of nanocomposites Fe(Co)-W corrosion resistance. *International Multidisciplinary Scientific GeoConference Surveying Geology and Mining Ecology Management, SGEM*, 2019, 19(6.1), pp. 19–25.