Transactions of the **13th International Conference on Structural Mechanics in Reactor Technology** (SMiRT 13), Escola de Engenharia - Universidade Federal do Rio Grande do Sul, Porto Alegre, Brazil, August 13-18, 1995

Substitution of cobalt alloying in PWR primary circuit gate valves

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ABSTRACT : The object of this study is to qualify cobalt-free alternative alloys for valve applications. This paper focus on tribological characterization of numerous coatings deposed by different process. Two tribometers are used. A selection of best coatings is done by using the first one, of a classical type. Then tests are performed with the second one which simulates sollicitations supported by gate valves in primary circuit of PWR. 35%Ni-Cr - 65%Cr3C2 coating, deposed by detonation gun technology, gives us hope to find a substitute of Stellite 6.

1. Introduction.

The presence of Cobalt in the primary circuit of Pressurized Water Reactor (PWR) is a major cause to primary circuit activity level. There are two main sources of cobalt in primary circuit materials [1]:

- Impurities in components such as steam generator tubes (Inconel 690, Inconel 600, Incoloy 800) and pipeworks (austenitic stainless steel).
- Principal alloying element in Stellite (hardfacing material).

The two major uses of Stellite, in the primary circuit, are in control rod drive mechanisms and in valves. The object of this study is to qualify Cobalt-free alternative alloys for valve applications.

The main difficulty is to find another coating alloy which have as good properties as Stellite in the point of view of corrosion, thermal chocs, friction and wear. So, numerous materials and coating processes are investigated. Their main characteristics are summarized in table 1.

Coatings	Substrate	Coating processes	thickness µm	hardness
Stellite 6	304 L	PTA	>2000	450 Hv$_{0.5}$
Inconel 625-X% NbC*	304 L	PTA	>2000	275 to 400 Hv$_{0.5}$**
Nitronic60-X% NbC*	304 L	PTA	>2000	300 to 450 Hv$_{0.5}$**
Cr-C (1.6 at%de C)	17-4-PH	PVD	1 et 4	1000 Hv$_{0.5}$
Cr-C (9.5 at%de C)	17-4-PH	PVD	1 et 4	1500 Hv$_{0.5}$
Cr/Cr-C/Cr/Cr-C	17-4-PH	PVD	2 et 8	1000 Hv$_{0.5}$
80%Cr_3C_2-20%(Ni - Cr)	17-4-PH	DG	100 et 200	800 Hv$_{0.3}$
65%Cr_3C_2-35%(Ni - Cr)	17-4-PH	DG	100 et 200	700 Hv$_{0.3}$
70%WC-25%Cr_3C_2-5%Ni	17-4-PH	DG	100 et 200	1100 Hv$_{0.3}$
80%Cr_3C_2-20%Inconel 625	17-4-PH	SDG	100 et 200	850-1100 Hv$_{0.3}$

Table 1: principal coating characteristics.
** X=10, 20 and 30*
*** Increasing with X*
PTA : Plasma Transferred Arc.
PVD : Physical Vapour Deposition [2].
DG and SDG : Detonation Gun technologies [3].

Qualification of these coatings is made in two steps. In a first hand, friction coefficient and wear rate are measured on plan/plan tribometer in atmospheric pressure and room temperature water. These data allow us to select coatings which have equivalent or better properties than those of Stellite. In a second hand, the selected coatings are tested in a tribometer which simulates the sollicitations supported by gate valves in a primary circuit of PWR.

2. First characterisations.

2.1. *Experimental apparatus.*

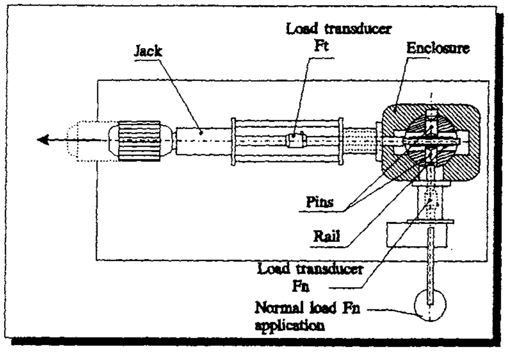


Figure 1 : *MEF tribometer(Ower view.)*

The tribometer (figure 1) is made up of one enclosure in which are introduced demineralised water, at atmospheric pressure and ambiant temperature, and samples (2 pins and 1 rail). With a normal quasi-static strenght (Fn) applied on pins, a tangential strenght (Ft) is necessary to move the rail. The speed of motion is 10 $mm.s^{-1}$ and its amplitude is 35 mm. The two contact pressures tested are 50 and 100 MPa. Friction coefficient (Cf) is calculated with Fn and Ft by :

$$Cf = \frac{|Ft|}{2 \cdot Fn}$$

The wear is controled measuring dimensions shown in the figure 2, each 100 to 200 cycles.

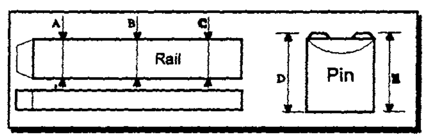


Figure 2 : *Illustration of control points on samples.*

2.2. *Friction.*

Several parameters can influence the friction of coated surfaces [4] : contact pressure, roughness of friction surface, substrate hardness, friction stability during cycling and coating material. Study of all these parameters have only could be realised on DG and Stellite 6 coatings. Other coatings have not be able to support friction conditions. PVD coatings have cracked under the load and surface fatigue. PTA coatings (Inconel 625 + X% of NbC and Nitronic 60 + X% of NbC with X=10 and 20), have been damaged by adhesion and abrasion phenomena.

Concerning DG coatings, roughness and substrate hardness have no significant influence on friction coefficient (figure 3 and 4).

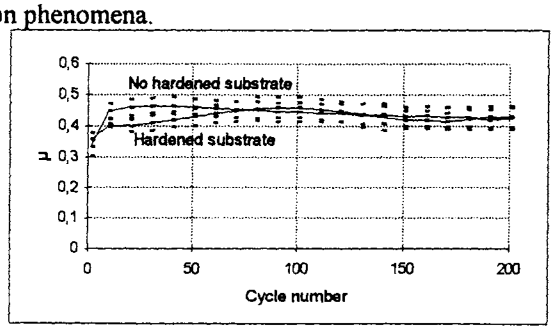


Figure 3 : *Substrate hardness influence on the 20%Ni-Cr - 80%Cr_3C_2 friction after numerous tests which added 500 cycles. The roughness is 0.1 μmRa and the contact presure is 100 MPa.*

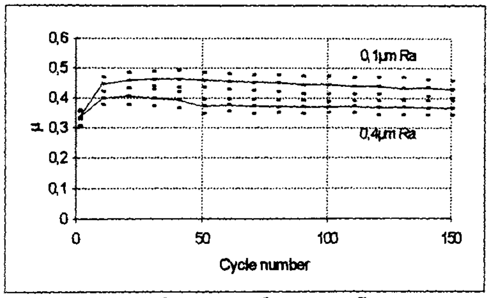


Figure 4 : *surface roughness influence on the 20%Ni-Cr - 80%Cr_3C_2 friction after numerous tests which added 500 cycles. The substrate is not hardened and the contact presure is 100 MPa.*

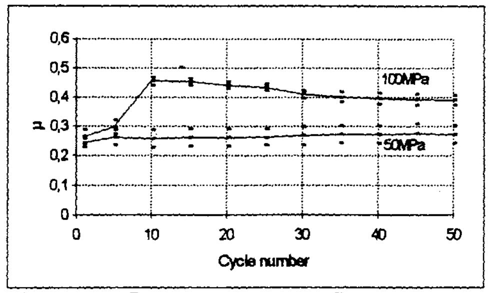


Figure 5 : *Contact presure influence on the 35%Ni-Cr - 65%Cr_3C_2 friction. The substrate is not hardened and the surface roughness is 0.4µmRa.*

For DG coatings, contact pressure augmentation cause, growth of friction coefficient (figure 5). For Stellite 6 coating, an opposed phenomenon is observed (figure 6).
Friction of this coatings is more or less stable, but the fluctuation never exceed 0.1 on friction coefficient (figure 7). So, same accommodation mechanisms, as defined by Berthier [5], are actived during friction.

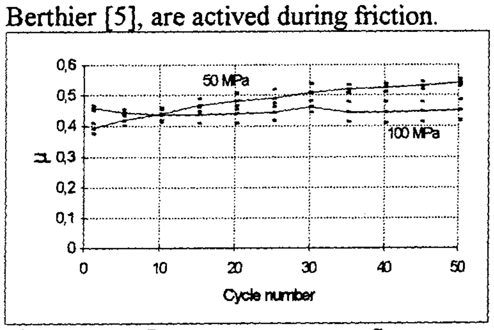


Figure 6 : *Contact pressure influence on the Stellite 6 friction.*

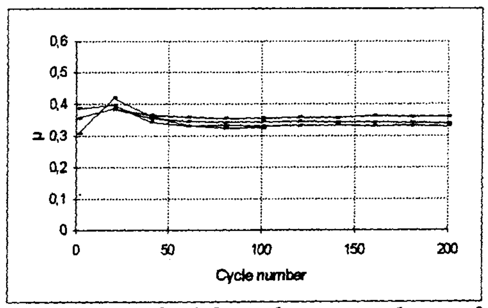


Figure 7 : *Stability during cycling of 20%Inconel 625 - 80%Cr_3C_2. Graphes, obtained during numerous tests realised in same conditions, are superposed.*

Figure 8 shows the friction performances of each studied coating. For this friction conditions, DG coatings are equivalent or better, according to their composition, than Stellite 6 coating.

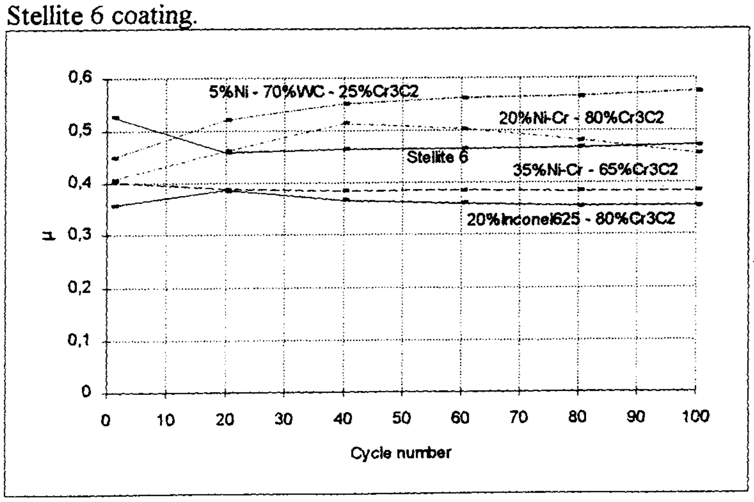


Figure 8 : *Friction performance comparison between each studied coating. Contact presure is 100 MPa.*

2.3. *Wear.*

The same parametric study is made for wear. Generaly, high friction surface roughness involves high wear, due to the removal of the top of asperities. The substrate hardness have small influence on wear, but, for hardest coatings, a hard substrate increases wear. The figure 9 shows wear performances of each studied coatings. The DG coatings are almost always better than Stellite 6 coating.

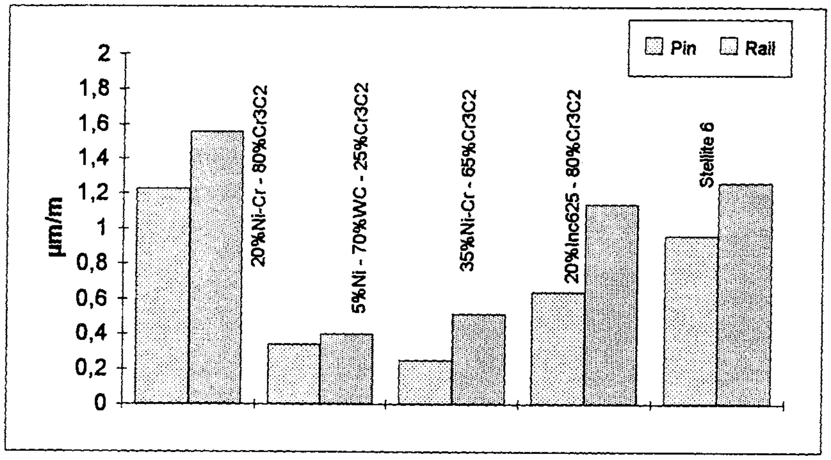


Figure 9 : *Wear of different studied coatings. The DG coatings substrate is not hardened and the surface roughness is 0.4 µmRa. Wear is presented by the ratio of depth used (figure 2) by the convered length.*

3. Tribological study.

Data, obtained in chapter 2, allow us to select coatings which have equivalent or better properties than those of Stellite 6. The three selected coatings are : 20%Ni-Cr - 80%Cr_3C_2, 35%Ni-Cr - 65%Cr_3C_2, 20%Inconel 625 - 80%Cr_3C_2.

3.1. *Experimental apparatus.*

The coatings are now tested on a tribometer which simulates the sollicitations supported by gate valves in a primary circuit of PWR (figure 10).

This apparatus represents half of a gate valve and it allows to make one coating disc slide on one coating seat. Each couple of disc and seat is characterized by friction coefficient, wear rate and watertightness of the sliding surfaces, in function of pressure and temperature of water in the enclosure.

Tribometer OPERA

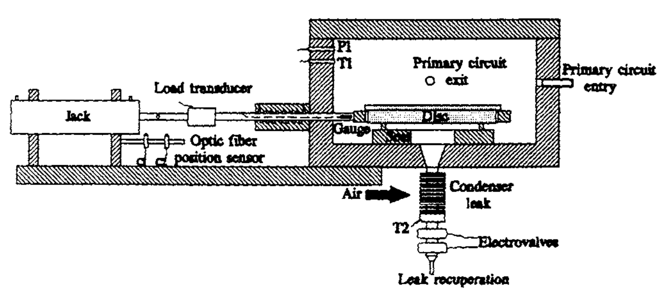


figure 10 : *tribometer*

The disc move alternatively on the seat at 10 mm.s^{-1} with an amplitude of 10 mm. A primary circuit pressure equal to 16 MPa (resp. 8 MPa) creates a contact presure equal to 100 MPa (resp. 50 MPa).

3.2. *Friction.*

Several conditions of primary circuit pressure and temperature have been tested with this tribometer. Only one parameter is influent on the friction coefficient : The temperature.

3.2.1. *Temperature influence.*

Temperature augmentation has two types of influence on the friction according to the coating.
For DG coatings, increasing of friction coefficient value, between ambiant temperature and 350°C is equal to 0.15 for 20%Inconel 625 - 80%Cr_3C_2 (figure 11), 0.1 for 20%Ni-Cr - 80%Cr_3C_2, and is not significant for 35%Ni-Cr - 65%Cr_3C_2 (figure 12).

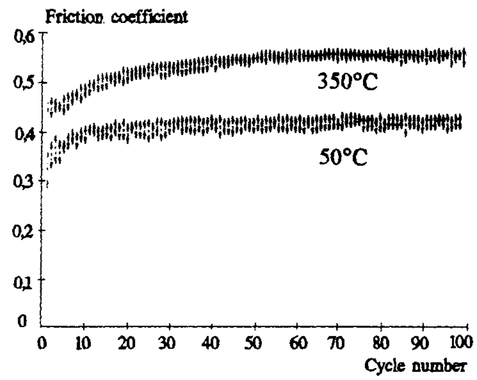


Figure 11 : *Temperature influence on 20%Inconel 625 - 80%Cr_3C_2 coating.*

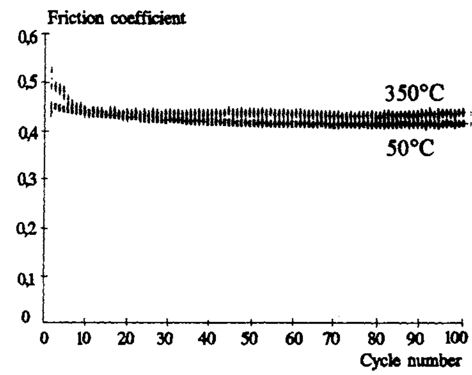


Figure 12 : *Temperature influence on 35%Ni-Cr - 65%Cr_3C_2 coating.*

At the opposite, Stellite 6 coating friction coefficient decreases with growth of temperature. The variation on friction coefficient between ambiant temperature and 350°C is equal to 0.2 (figure 13).

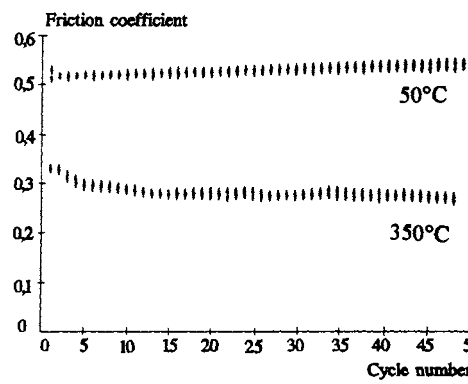


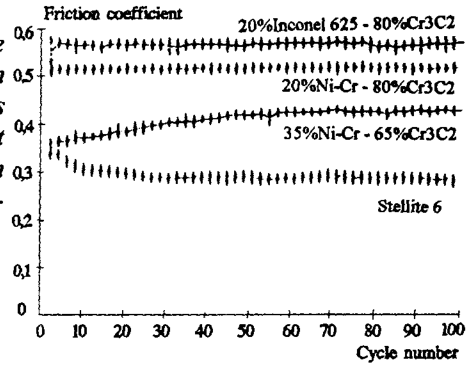
Figure 13 : *Temperature influence on Stellite 6 coating.*

3.2.2. *Coating performances.*

All these coatings show a good stability during the friction tests. In conditions of ambiant temperature and 16 MPa of primary circuit pressure, same results than those found in chapter 2 are obtained. But, if temperature increases until 350°C, friction coefficient value changes (figure 14). Indeed, Stellite 6 coating, which has the worst friction coefficient at ambiant temperature, has the best one at 350°C.

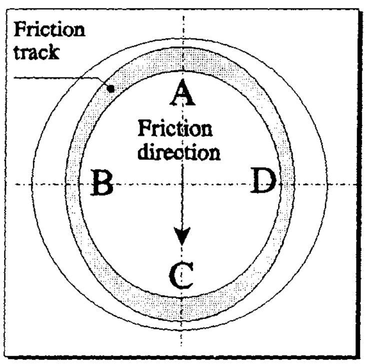
The best friction behaviour for DG coatings, is the one of 35%Ni-Cr - 65%Cr_3C_2. In comparison with the others DG coatings, we can write that Molybdenium and Fe additions in Ni-Cr binding (difference between Ni-Cr and Inconel 625 bindings) reduce friction at ambiant temperature but increase it at 350°C. Moreover, the augmentation of Ni-Cr binding proportion in comparison with carburized phase (difference between coatings with Ni-Cr binding), desensitize the friction to the temperature.

Figure 14 : *Friction performance comparison of each studied coating on OPERA tribometer. The test conditions are 350°C and 16 MPa of primary circuit presure. The lowest to the highest friction coefficient, we can see : Stellite 6, 35%Ni-Cr - 65%Cr_3C_2, 20%Ni-Cr - 80%Cr_3C_2, 20%Inconel625 - 80%Cr_3C_2.*



3.3. *Wear.*

The wear evaluation is made by the loss of thickness on seat and disc surfaces. Wears of different coatings during friction tests are between 50 and 120.10^{-3} µm/cycle for the seat and between 10 and 14.10^{-3} µm/cycle for the disc (figure 16).



On the disc, two zones (AC and BD) can be distinguished (figure 15). As shows the roughness profil of friction surface, wear tracks on B D zones are more deep and narrow than A C zones. Two coatings have got the similar best wear performance : 35%Ni-Cr - 65%Cr_3C_2 and 20%Ni-Cr - 80%Cr_3C_2.

Figure 15 : *Wear track on the disc. BD zones are much deep and straight than AC zones.*

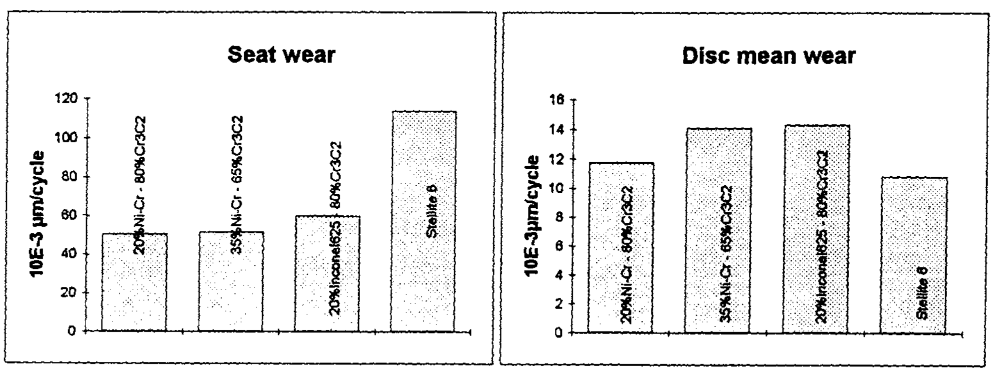


Figure 16 : *Wear of seat and disc for different coatings.*

3.3. *Watertightness of sliding surfaces.*

The watertightness evolution of sliding surfaces during tests is too variable to be easily correlated to wear. None of the coatings have warranted a leak lower than 7.5 $ml.h^{-1}$, which is the leak criterion imposed before all friction. It is only after grinding of some friction cycles that the leak criterion have been satisfied. The leak criterion fixed for surfaces who have slided more than 1500 cycles is 22.5 $ml.h^{-1}$.

The leak evolution during cycles is described in table 2. Vapor leak, for tests realised at high temperature, can not be measured. But it is much higher than the second leak criterion.

Coatings	**Leak in $ml.h^{-1}$**
20%Ni-Cr - 80%Cr_3C_2	5 à 10
35%Ni-Cr - 65%Cr_3C_2	7 à 8 until 1250 cycles then 90 after 1650 cycles
20%Inconel 625 - 80%Cr_3C_2	8 à 16 until 600 cycles then vapor leak.
Stellite 6	8 until 500 cycles then vapor leak.

table 2 : *leak evaluation during the life of different samples.*

We can observe that coatings who give the best result in wear, have the lowest leak.

3. Conclusion.

In the first tribological characterization, we show that selected PVD coatings are not adapted for nuclear valve applications. Moreover, PTA coatings, except Stellite 6, have been damaged by adhesion and abrasion after few cycles. Only DG coatings and of course Stellite 6 coating have been characterized. During tests, parametric study is made. We show that for DG coatings, surface roughness and substrate hardness have little influence on friction. Wear is increased by a high routhness.

With the tribometer OPERA, which simulate gate valves sollicitions, we show the great influence of temperature on friction. To obtain lower friction coefficient in PWR primary circuit pressure and temperature conditions (350°C and 16 MPa), the best DG coating composition is 35%Ni-Cr - 65%Cr_3C_2. It can be noticed that wear of disc is not homogeneous but lower than the wear of seat.

With regard to watertightness of sliding surfaces, the lowest leak is obtained with coatings which have the lowest wear. 35%Ni-Cr - 65%Cr_3C_2 coating is included in them.

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