ISSN : 0974 - 7486 Volume 13 Issue 11

Materials Science

An Indian Journal

Full Paper

MSAIJ, 13(11), 2015 [347-352]

Effect of the chromium content on the room temperature hardness of binary cobalt-based, nickel-based and iron-based cast alloys

Patrice Berthod, Elodie Conrath

University of Lorraine, Faculty of Sciences and Technologies, Institut Jean Lamour (UMR 7198), Team 206 "Surface and Interface, Chemical Reactivity of Materials", B.P. 70239, 54506 Vandoeuvre-lès-Nancy, (FRANCE)

E-mail: patrice.berthod@univ-lorraine.fr

ABSTRACT

Many superalloys contain high quantities in chromium to resist hot oxidation and corrosion. Sometimes partly involved in carbides, the great majority of the Cr atoms are stocked in the matrix of the cobalt-based alloys, the iron-based ones, and some of the nickel-based alloys not too rich in aluminium. The presence of several tens percents of chromium in tha matrix may change its hardness. This work, carried out on binary M-xCr alloys (M=Co, Ni or Fe; x varying between 0 and 33 wt.%), shows clear hardening effect of the chromium present in solid solution. For example the Vickers hardness of cobalt rises of one hundred points from 0 to 33 wt.%Cr. Similar effect exists for nickel while the dependence of the iron hardness on the chromium content is not monotonous.

© 2015 Trade Science Inc. - INDIA

KEYWORDS

Chromium;
Hardness;
Cobalt alloys;
Nickel alloys;
Iron alloys.

INTRODUCTION

With aluminium and silicon, chromium is one of the most important element belonging to the chemical composition of superalloys[1-4]. Indeed it brings these exceptional refractory alloys remarkable resistance against high temperature oxidation by gases and corrosion by aggressive molten substances[5, 6]. When added to these alloys in sufficient quantities it allows the development and the maintenance of a continuous oxide scale all around pieces, chromia (Cr_2O_3). Although less efficient than alumina (Cr_2O_3) as barrier for the O^{2-} anions and metallic cations, this chromia oxide significantly limits this ionic diffusion and then slows down the oxidation progress and the alloy deterioration, and delays the catastrophic oxidation. Chromia is especially efficient in enhancing the resistance against corrosion by molten salts or glass, more than alumina.

Often present with contents of several tens of weight percents in the cast cobalt-based, iron based and nickel-based alloys to allow them behaving as chromia-forming alloys, chromium may also influence the hardness of the alloys. This is first evident when chromium is partly present as carbides[7-9] but such effect is possible when chromium is present in solid solution in the matrix of the alloy.

The purpose of this work is to specify how the chromium content may specifically influence the hardness at room temperature of the matrix of cobalt-based, nickel-based and iron-based alloys by elaborating binary alloys with increasing Cr contents and testing them in micro-indentation and macro-indentation.

EXPERIMENTAL

Pure elements (Co, Ni, Fe and Cr, mainly Alfa Aesar, purity > 99.9wt.%) were melted together in a CELES high frequency induction furnace under inert atmosphere (300 mbars Ar) in a water-cooled copper crucible isolated from the laboratory air by a silica tube. The alloys were maintained in the liquid state during three minutes after melting to ensure complete chemical homogenization before solidification and solid state cooling. The obtained ingots, the Cr contents of which varied from 0 to 33 wt.%, were then cut and imbedded in a cold resin mixture (resin CY230 and hardener HY256). They were ground with SiC papers from 240-grit up to 1200-grit.

The less Cr-rich alloys (re-melted and solidified pure Co, pure Ni and pure Fe) and the Cr-richest ones (containing 33wt.%Cr) were subjected to Vickers micro-indentation (load 32g) and macro-indentation (10kg) during varying durations (1s, 10s, 40s, 100s) to explore the possible effect of the duration on the hardness result and select a final indentation duration for all the alloys. Thereafter three 32g-load and three 5kg-load Vickers indentations were performed per alloy to obtain an average value and a standard deviation value. The used apparatus were a Reichert model 32 one for micro-indentation and a Testwell Wolpert one for the macro-indentation.

RESULTS AND DISCUSSION

Preliminary tests: effects of the duration

Initially, a preliminary short study of the

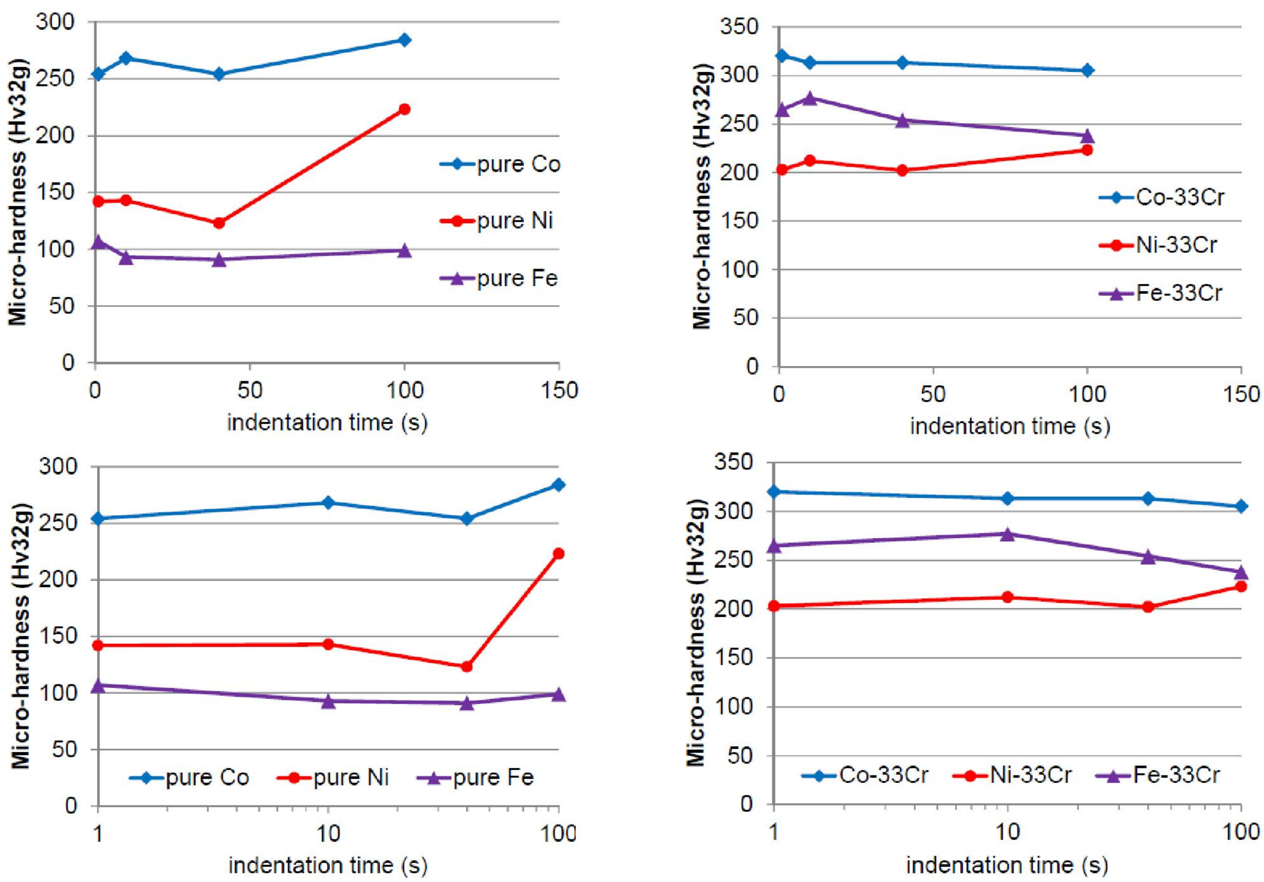

Figure 1 : Evolution of the measured Vickers micro-hardness measured with the duration of application of the maximal load (32g); left: case of the three chromium-free alloys, right: case of the three chromium-richest (33wt.%Cr) alloys (top: linear abscissa; bottom: logarithmic abscissa)

dependence of the obtained hardness value on the duration of maximal load appliance was realized. This aimed to first observe how fast the indentor penetrates in the studied alloys and at which time it stabilizes, and second to select a constant time for all the following tests. This was done for the micro-indentation under 32g and for the macro-indentation under 5kg, for the three studied families of alloys but only for the two extreme values of chromium content, 0 and 33wt.%, which may lead to extreme values of hardness per family..

The results obtained for micro-indentation are graphically presented in Figure 1-left for the M-0Cr (M=Co, Ni or Fe) and Figure 1-right for the M-33wt.%Cr alloys. They are not really clear by the way that two of the three variations are rather difficult to interpret. In the case of pure Fe duration of 1 second is not long enough and one can think that the viscoplastic deformation is still running; stopping the load application interrupts the penetration with as result a pyramidal cavity smaller than after longer load application. The resulting hardness value appears higher than real and is overestimated. Longer duration leads to lower values which are close to one another, this demonstrating that 10 seconds are enough. The results obtained for pure Co and pure Ni are more scattered and difficult to interpret, especially the high values of hardness after 100s.

Similar comments may be globally done about the results of micro-hardness obtained for the Cr-richest alloys. One can see that 10 seconds may be a good standard duration value: the 32g load will be thereafter systematically applied for the micro-indentation of the other alloys.

The same preliminary tests concerning the possible influence of the indentation duration were performed for the as-called “macro-indentation” (i.e. under 5kg). The results, shown in Figure 2-left (pure Co, Ni and Fe) and in Figure 2-right (Cr-33wt.%Cr), suggests that the values measured after

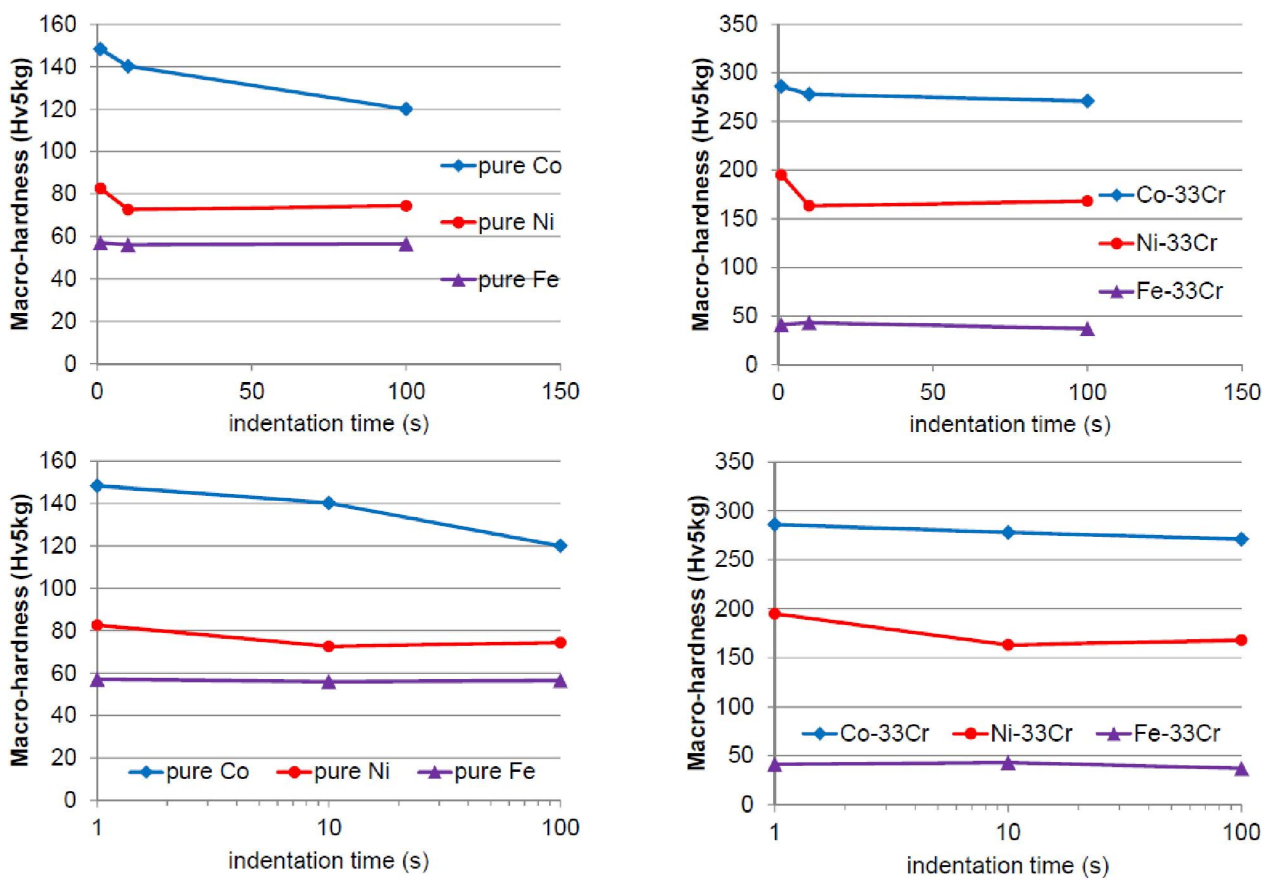

Figure 2 : Evolution of the measured Vickers macro-hardness measured with the duration of application of the maximal load (5kg); left: case of the three chromium-free alloys, right: case of the three chromium-richest (33wt.%Cr) alloys (top: linear abscissa; bottom: logarithmic abscissa)

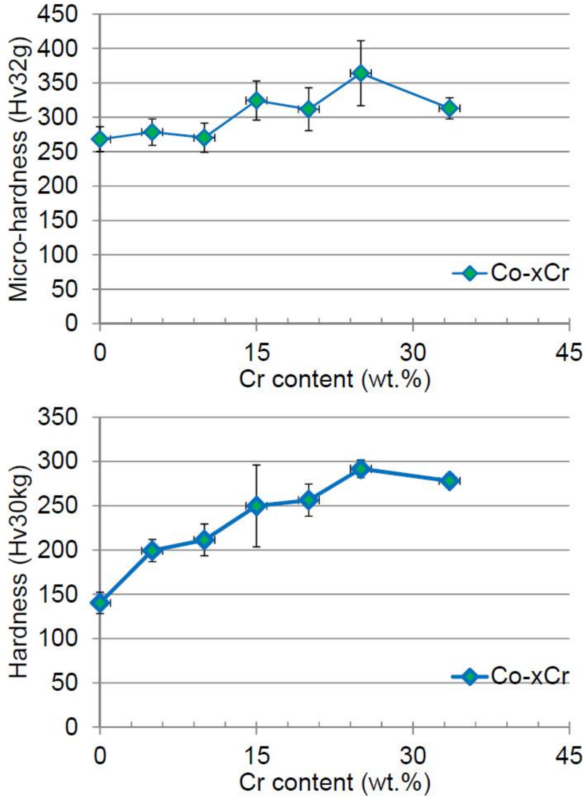

Figure 3 : Evolution of the measured Vickers micro-hardness (top) and of the measured Vickers macro-hardness (bottom) with the increase in chromium content in the case of the cobalt-base binary alloys

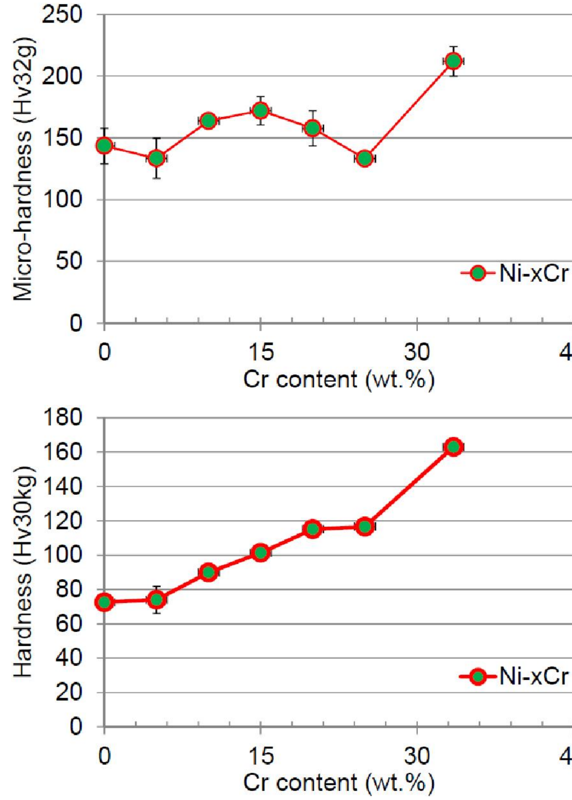

Figure 4 : Evolution of the measured Vickers micro-hardness (top) and of the measured Vickers macro-hardness (bottom) with the increase in chromium content in the case of the nickel-base binary alloys

only 1s of load-application risks to lead to overestimated hardness while 10s is long enough to give a reliable value, in most cases (only one exception: pure Co). It was thus chosen to apply the load during ten seconds for all micro- and macro-indentation tests.

Micro- and macro-hardness of the cobalt-base binary alloys versus their chromium content

Obviously the micro-hardness of the cobalt-based alloys increase with the chromium content, at least until reaching 25wt.% Cr (Figure 3 top). One hundred Hv32g points more (micro-hardness varying from about 270 to about 370) are monotonously obtained by progressively adding 25 wt.% to pure cobalt. After, with the Co-33wt.%Cr alloy, the micro-hardness falls a little. The macro-hardness follows exactly the same trend (Figure 3 bottom) but with lower values (start at about 140 only and increase up to about 290 for 25 wt.% Cr).

Micro- and macro-hardness of the nickel-base binary alloys versus their chromium content

The macro-hardness of the nickel-base alloys also increases regularly, here over the whole chromium content range (Figure 4 bottom). Adding chromium promotes hardening from about 70 up to about 160 Hv5kg for the Ni-33 wt.%Cr alloy. In contrast, the micro-hardness values, here too higher than the macro-hardness ones, are much more scattered in term of reproducibility for a given alloy and in term of regularity of variation versus the chromium content (Figure 4 top)

Micro- and macro-hardness of the iron-base binary alloys versus their chromium content

For the iron alloys a lack of monotony versus the chromium content affects both the micro-hardness results (Figure 5 top) and the macro-hardness ones (Figure 5 bottom).

Comparison of the micro- and macro-hardness of the three families for the studied chromium range

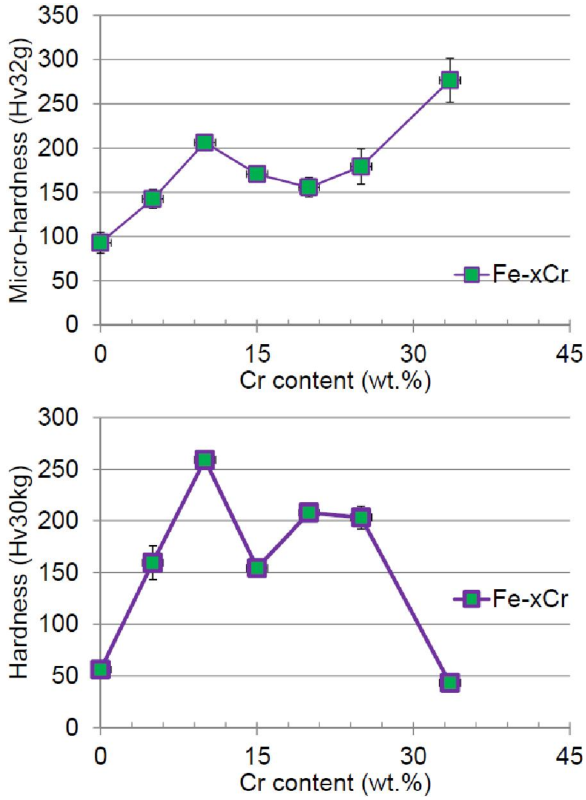

Figure 5 : Evolution of the measured Vickers micro-hardness (top) and of the measured Vickers macro-hardness (bottom) with the increase in chromium content in the case of the iron-base binary alloys

The micro-hardness results are all plotted together versus the chromium content in Figure 6. It is clear that the binary cobalt alloys are all significantly harder than the other alloys whatever their chromium contents. The iron-based alloys seem to be a little harder than the nickel-based ones containing the same chromium quantity. This is the same hierarchy which seems existing among these three families for the macro-hardness (Figure 7).

General commentaries

The chromium content has obviously a great influence on the hardness of these binary alloys. In the cases of the binary cobalt-based alloys and of the nickel-based ones the presence of chromium clearly enhances the hardness and this one rather regularly increases with the chromium content on the whole studied range of chromium content. This is true for both micro- and macro-hardness for the cobalt alloys and more for the macro-hardness of the nickel alloys. The presence of chromium atoms

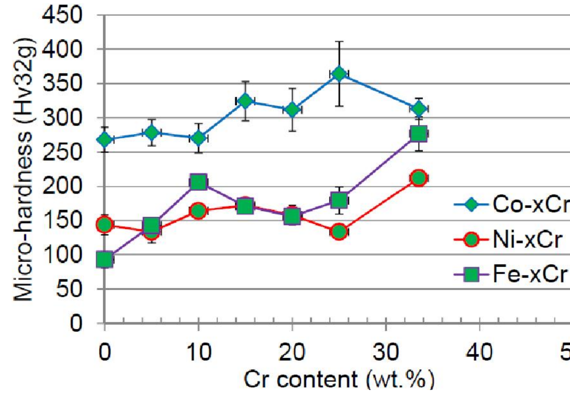

Figure 6 : Evolution of the measured Vickers micro-hardness of the three types of binary alloys versus the chromium content

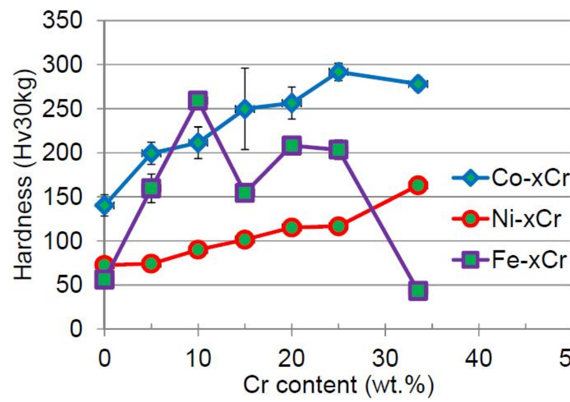

Figure 7 : Evolution of the measured Vickers macro-hardness of the three types of binary alloys versus the chromium content

in solid solution clearly hardens the alloys of these types, as well as it probably strengthens them a little for use at high temperature under stresses. The variability of the micro-hardness of the nickel alloys remains however to be explained. The curious variation of the hardness, micro or macro, of the iron alloys versus the chromium content are maybe explainable by the alpha-favouring effect of chromium which did not allowed the possible maintenance of a part of austenitic crystalline network with which the chromium-poorest alloys probably solidified and cooled in a first time. Indeed it is possible that the fast cooling due to the small size of the ingots and to the copper crucible effectively led to the persistence of this harder face centred cubic phase while the ferritic body centred cubic phase was favoured the high contents in chromium in the Cr-rich iron alloys for its appearance instead the FCC phase during cooling and even at solidification for the Cr-richest alloys. This is to be verified by X-ray diffraction. The systematically higher values obtained by micro-indentation than the ones obtained by macro-indentation, maybe due to the {formed cavities / grain size} ratii, however remains to be interpreted.

CONCLUSIONS

Thus, despite their proximities in the Mendeleiev's periodic table the chromium atoms induce significant hardening to the cobalt-based and nickel-based alloys, with probably the same effect for the room temperature hardness of the whole alloys the matrixes of which may be constituted of these binary alloys. This was clearly revealed here by these investigations on simple cast alloys for which no possible stressed state induced by cooling because the presence of interdendritic carbides for example may be evocated to explain such variations for the micro-hardness values, and for which macro-indentation was possible on single-phased alloys (supposed single-phased in the case of the Fe-base alloys maybe constituted of ferrite and austenite simultaneously, and also for the Co-base alloys which can be both austenitic and hexagonal). Before being strengthened and then hardened by heavy atoms in solid solution and/or by precipitated secondary carbides or hard intermetallic particles, the sometimes high weight contents in chromium devoted to the chemical resistance at high temperature of some superalloys may participate to the high temperature strength, but also to the low temperature lack of machinability.

REFERENCES

[1] C.T.Sims, W.J.Hagel; 'The superalloys', John Wiley and Sons, New York, **(1972)**.

[2] A.M.Beltram, in C.T.Sims, N.S.Stoloff, W.C.Hagel; 'Superalloy II – High temperature materials for aerospace and industrial power', John Wiley, 135 **(1987)**.

[3] E.F.Bradley; 'Superalloys: A Technical Guide" (1st edition), ASM International, Metals Park, **(1988)**.

[4] M.J.Donachie, S.J.Donachie; 'Superalloys: A Technical Guide" (2nd Edition), ASM International, Materials Park, **(2002)**.

[5] P.Kofstad; 'High temperature corrosion', Elsevier applied science, London, **(1988)**.

[6] J.Young; 'High temperature oxidation and corrosion of metals', Elsevier, Amsterdam, **(2008)**.

[7] P.Berthod; Materials Science and Technology, **25(5)**, 657 **(2009)**.

[8] P.Berthod; Materials Science and Technology, **25(5)**, 663 **(2009)**.

[9] P.Berthod; Materials Science and Technology, **25(8)**, 1003 **(2009)**.