Abstract

The assembly of various materials by the conventional methods finds its limits in certain specific applications. We approach a study on the solid state diffusion bonding between zircaloy (Zy₄) and stainless steel (304L) for an application in the sector of the nuclear power.

The diffusion couples prepared underwent treatments at the temperatures ranging between 850°C and 1020°C in a controlled atmosphere and under dynamic pressures of contact. We give a particular attention to the morphology of the interface, formed, with the chemical reactions of exchange which proceed between two entities Zy₄/304L like with the determination of the nature of the compounds formed with the interface. The observations and chemical analysis are realized by optics microscopy's and electronics (ESEM-EDX) and with X ray diffraction (XRD). The quantitative distributions as well as the detailed localization of the basic chemical elements are defined by chemical profiles, characteristics of each element. The junction with the interface of diffusion consists of three zones distinct, formed from a solid solution αFeCr, rich in Cr in the form of a homogeneous edge, localized in steel side. The zone of the center and that of side Zy₄ are two-phase. They are made up, for one, of αFeCr-Zr(Fe,Cr)₂ and for the other, Zy₄ side, the solid solution αZr and the intermetallic compound Zr₂(Fe₁₋ₓNiₓ) where X is understood enters 0,15 and 0,25. The detailed results obtained, are a stepping, between those obtained from the observations and chemical analyses and radio crystallographic. The values of the measured microhardnesses give a very heterogeneous filiations to the level of the interface of the two entities.

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1. Introduction.

In the nuclear engineering, many parts in zirconium and its alloys, should be assembled with other materials, often in stainless steel [1,2]. The use of conventional techniques of assemblies such as the arc cuttings and of type TIG, are less employed. The assembly carried out, by these processes of partial fusion or total of materials to be
assembled, led to the brittleness of the weld which is due not only, to the metallurgical transformations induced within the thermally affected zones of the two entities to be welded, but also to the form of the interface being used as physical junction between these entities, in which hard intermetallic compounds are formed close to a matrix out of balance. These phenomena are undesirable in the industry because they can lead to undesirable consequences [2,3].

Indeed, works carried out on the joints welded by the (TIG) process between alloy of Zr of Zy4 type and stainless steel 304L [4], indicate that the intermetallic compounds formed at the interface are of the type Zr(Cr, Fe)2, and Zr2Fe - Zr2Ni in eutectic form. They also indicate that the compound Zr(Fe, Ni)2 is located near the molten zone of Zy4 side, and that its density is approximately twice larger compared to the eutectic phase Zr2 Fe - Zr2 Ni. Other works [5] on the electron beam welding between the stainless steel and zircaloys-4 also indicate, the presence of fragile intermetallics of the type Zr(Cr, Fe)2 in the level of their interface.

The tracing of the Zr-Fe system, used as reference for the study of binary alloying, envisages the formation starting from the liquid state, of stoichiometric definite compounds of Zr2Fe types and Zr3Fe, in the rich side of zirconium, and ZrFe2 Zr6Fe23 of the rich side of iron [6].

The work of [7] on the elaboration of the Zr-8SS (SS304-92Wt%Zr) alloy, indicates the formation of the following phases: α Zr, Zr2(Cr, Fe), Zr2(Fe, Ni), Zr3 (Fe, Ni) and Zr(Cr, Fe)2. It mentions that at the temperature of 1020°C, the phase ZrFe2 is probably the phase of type Zr(Cr, Fe)2 and with 940°C, the phase Zr3Fe is probably Zr(Fe, Ni). It adds that the decomposition of small fractions of metastable compounds of Zr2(Fe,Ni) and Zr2(Cr, Fe), change respectively into Zr2(Fe, Ni) and Zr2(Fe, Cr) during cooling.

However, the metallurgical bonding obtained by interdiffusion of the chemical elements of share and others of the interface, in a solid state, represent solutions, often satisfactory in the assembly of these two materials in the field of the nuclear power. Among those, bonding diffusion is the technique, most employed for this kind of bonding.

This process takes place in solid phase in which the parts are maintained in mechanical contact under given pressure and are brought up to a defined temperature, during a given time. This leads to an intimate contact of surfaces and to a chemical migration, thermically activated of the elements, what makes it possible to obtain, at the end of the cycle, a junction between the antagonistic parts [8].

The interaction between the stainless steel and Zr alloy, obtained by solid state diffusion bonding, with or without intermediate metals, has already made the object of various works [9-12]. Certain authors [9] used the Nb, Cu and Ni elements, as intermediate metals, and concluded that no intermetallic compound was formed on the level of the junction. Other authors [10], interpose Ti, and they noted that this element forms a barrier preventing the diffusion of Fe, Cr, Ni and Mo towards Zy-4 and that none of intermetallics compounds of Zr(Cr, Fe)2, Zr2Fe and Zr2Ni has been observed.

The study of the diffusion of the components of the entities welded at the interface formed and the nature of the phases formed, between the stainless steel and zirconium alloy, welded by diffusion without intermediate metals, are few available in the literature. Certain published works [11] noted the presence of the binary intermetallic compounds of the type, ZrCr2 Zr2Fe and Zr2Ni, at the interface of Zy2 / steel, with the formation a rich zone of Cr, in stainless steel side. On the other hand, these last (Zr2Ni and Cr) compounds are not mentioned in other works, of the diffusion bonding [12]. In addition to the intermetallic compound of ZrCr2 type, these authors propose a zone of diffusion containing another compound called, "X" not identified and that they suppose it, of ternary nature between the Zr-Fe-Ni elements. The presence of this compound was also reported in other work [4].

The interpretation of the nature of these compounds formed in the presence from a molten liquid fraction, then solidified, is based on the reading of the binary systems (Fe-Zr, Zr-Cr, Zr-Ni) and ternary systems (Zr-Fe-Cr, Zr-Fe-Ni). These systems are complex and not very available in the literature. They serve as basic models at the interpretation of solidification allowing the knowledge of the formed compounds nature.

Indeed, in work of [13], on the Zr-Fe-Ni system, it is indicated that there is a disagreement on miscibility between the Zr2Ni and Zr2Fe binary compounds. For certain authors, miscibility is total between these compounds, and the field of the considered phase extends towards two (Fe2Zr + (Fe,Ni)Zr2 phases binary and for the others, they indicate that the existence of two distinct compounds which are Zr2(Ni1-x Fex) and Zr2(Fe1-x Nix). The presence of Ni in these alloys is favouring the formation of Zr2(Ni1-x Fex) and Zr2(Fe1-x Nix) compounds.

As for the results of the works obtained by [13] during the elaboration of the composition Zr2 Fe16.4 Ni16.5 alloys, these authors reveal the presence of two phases. Among elaborate alloys, some of them have been partially
oxidized. The results of these alloys indicate only the presence of two phases of \( \text{Zr}_2(\text{Ni}_{1-x} \text{Fe}_x) \) and \( \text{Zr}_2(\text{Fe}_{1-x} \text{Ni}_x) \) type, where \( 0.15 \leq x \leq 0.25 \). Consequently, these authors have not detected the presence of a ternary compound.

Moreover, in the attempt of the layout of the Zr-Fe-Ni system ternary diagram presented in the work of [4], it is mentioned that only the binary compounds are formed and that no ternary compound was highlighted.

The goal of our present work is to carry out Zy4/304L junctions, formed by diffusion bonding, between the two entities put in contact, at various temperatures and under a dynamic pressure. We study the morphology of the formed interface, by determining the distribution of the various constitutive chemical elements. These compounds are formed, thanks to the chemical reactions of exchanges which unroll by diffusion in a solid state, through, the interface separating the two welded entities that we characterize by the chemical profiles, and imagery X. The results obtained on the nature of the formed compounds by solid phase welding are compared and discussed in comparison with those available in the literature who base themselves, on the crystallization of composed starting from an molten liquid then solidified using the systems of balance binary and ternary, as interpretation bases.

### 2. Materials and experimental techniques

The zircaloy (Zy4) and stainless steel (304L) used for this study, are directly delivered from industry with chemical compositions deferred in the table1. The zircaloy contains a weak - tenor of Sn (1.4 %), and of Fe (0.24 %). Stainless steel 304L contains a high concentration of Cr (18 %) and Ni (9.5 %) with a weak carbon concentration of (0.03 %).

| Alloys   | Elements | Fe  | C   | Zr  | Cr  | Ni  | Sn  | O   |
|----------|----------|-----|-----|-----|-----|-----|-----|-----|
| 304L base|          | 0.03| -   | 18  | 9.5 | -   | -   | -   |
| Zircaloy-4|          | 0.24| 130ppm| base| 0.085| -   | 1.4 | 1100ppm |

Samples of 08 mm in diameter and 5 to 7 mm height were prepared by cutting from larger pieces. There have been then machined, rectified polished with the emery paper of 1200 rank, degreased and cleaned with acetone in an ultrasound tank and then dried. Welding is carried out by means of a unit realized at the laboratory. Its functionality has already been tested in former work [14]. It comprises two parts: One is composed of a pneumatic jack coupled to a mobile axis, allowing to exert a pressure on the samples to be welded; the other part is used as support for the specimens to be assembled. This one is introduced into the vertical furnace of mark Adamel, of TV3 type, for treatments of the diffusion bonding solid state. The experiments of bonding are carried out under an atmosphere of argon, reaching temperatures of 850°C, 950°C and 1020°C that correspond to the \( a, a + \beta \) and \( \beta \) fields of Zr. The duration of the cycle of each treatment of diffusion is selected, constant of 45 minutes. The pressure exerted on the samples decreases with the increase of temperature because, the soften of zircaloy caused by the increase of temperature requires weaker pressures in order to avoid its crushing on the stainless steel with which it is put in contact. The pressure exerted on the couple of diffusion during the maintenance at various selected temperatures of 850°C, 950°C and 1020°C corresponding to pressures of 11.2 MPa, 2MPa and 0.8MPa respectively.

The characterization of the obtained junctions was initially carried out using an optical microscope for the preliminary observations. The samples were cut out longitudinally at the Zy4/304L junction, and were prepared by using the conventional metallographic techniques (polishing, cleaning...). The solution of the chemical attack used, to reveal the structures formed in the couples of welded samples is made up of: 47%HNO3 + 3% HF + 50% H2O2. The observations on fine ladder are carried out by using an electronic microscope with environmental sweeping (MEBE), with an emission fields gun of type XL30 of Philips mark, this equipment is coupled with a X-ray spectroscopy of type EDS of energy dispersion allowing punctual chemical analyses, and to observe the distribution and localization of various chemical elements in the diffusion zone.
The radio crystallography nature of the formed compounds is determined by the x-rays diffraction. The source used is a copper anticathode with a wavelength ($\lambda = 1, 54056 \, \text{Å}$), a tension of 40KV and an intensity of 40 mA.

The microhardness profile at the diffusion zone level and its surroundings is realized under a load of 0,5N by means of a microdurometer of MHT-10 mark incorporated in a optical microscope (Carl Zeiss Hall 100).

3. Results and discussion.

The junctions obtained at various temperatures, between steel and Zy4 are healthy. They do not contain no porosity or apparent vacuum. The microstructure of the couple of diffusion welded at various temperatures is reproducible in its tendency and its general form. We present, in what follows, the results obtained on the couple welded stainless Zy4/304L carried out at 1020°C which presents a broader interface made up of zones and compounds highlighted well and easily analyzable.

The interface gathers various phases formed by the chemical elements (table1), of the two entities put in contact: forming, by diffusion in a solid state, a thick interface. We retain, by advance, that the carbon contained in steel is in the form of stable metallic carbides and that Sn (1,4%) contained in Zy4 is completely put in solid solution in Zr. In the continuation of this work, we will not consider the possible effects of these two elements (carbon and Sn).

Each chemical element: Fe, Zr, Cr and Ni have an influence on the formation of the interface and the intermetallic compounds in its bosom, which is considered as follows. We present successively, the results obtained on the morphology of the interface, the repartition of the chemical elements, the nature of the formed phases and microhardness of the welded couple.

3. 1. Morphology of the interface Zy4/Stainless steel 304L

By using secondary contrasts of electrons with the MEB, the observations of this surface did not allow a clear description of the various zones formed in the interface. We have then chosen observations using electronic contrasts characteristics of the atomic number Z which is definitely variable between the various basic chemical elements of these alloys ($Z_{Fe}=24$, $Z_{Cr}=26$ and $Z_{Ni}=28$). These electronic contrasts highlight well the various entities formed, as well as their physical limits. Thus we could distinguish with the MEB that on both sides of 304L and Zy4 three distinct zones are characterized and represented on Figure 1a.

These zones do not clearly form separate linear limits. They present weak dilutions. They are illustrated in figure 1a for the case of the samples couple treated until 1020°C and which are:

Zone I is an edge of dark contrast adjacent to steel and it has a weak thickness, approximately 7μm. It is homogeneous and is located along the formed junction.

Zone II, pigmented, is of gray contrast. It is thicker approximately 45 μm. This zone appears a two-phase. It consists of polygonal fine grains encharged in one matrix of grey electronic contrast.

Zone III, of the side Zy4, is a area broader, of approximately 60μm thickness. It is made of clear gray small islands in a matrix of clear contrast, similar to that of Zy4 grains.

Here, it should be underlined that, the former works of diffusion welding between the stainless steel (304L) and of zirconalloys (Zy4 and Zy2) indicates that the interdiffusion of the chemical elements between the two entities, forms an interface composed of only two distinct zones [11,12]. The results advanced in works of [11] indicate that a zone of thickness of 8-9 μm of steel side, is rich in Cr, with Fe and Zr, and that the other broader of 60-70 μm, adjacent zone in Zircaloy, is composed of two phases: one gray contains (Zr, Fe, and Ni) and the other clear gray (Zr-Sn). Works of [12] indicate that the zone of the Zircaloy side is of a width of 30 μm is rich in Zr, and that the other of 40 μm broad, contains Cr, Fe and Ni. Its content of Cr, decrease suddenly on a depth of 10 μm to the profit of Zr. These results are in conformity with zones I and III which we observed. Zone II of the interface center that we have described, is not mentioned by these authors. This intermediate zone presents a form pigmented and two-phase can be confused with one of the other adjacent zones Figure 1a.

3.2. Repartition of the chemical elements to the interface

The quantitative distribution of the chemical elements to the interface is obtained by concentrations profiles which are carried in ordinates of figure 1b.
The concentration profiles of chemical elements Fe, Zr, Cr and Ni carried out on the welded samples with 1020°C are gathered in figure 1b. They indicate that in the steel side, a fast decrease of concentrations of Ni and the Fe, at the profit of the noticed increase in Cr, and the presence of Zr. Cr gives a culminating peak of 40% of its mass, thus creating one bordered which is like a diffusion barrier of Zr towards steel. This behavior was already observed by certain authors [10, 11 and 15]. On the other hand, other authors [12] do not mention it in their work. Moreover, the same behavior was also observed in other work [2] of diffusion welding between the stainless steel and Ti which also forms an edging of steel side. In a similar manner, Cr makes diffusion barrier for Ti. This result comes to confirm this tendency noticed, of the accumulation of Cr to the interface ZY₄ / 304L.

Fig. 1. A- Micrographies with the MEB, B- Concentration profile of the elements Zr(L/a), Cr(Kα), Fe(Kα) and Ni(Kα) and C- microhardnesses of the zones of diffusion of couple ZY₄ / 304L, bonded at 1020°C.
Beyond this area, which is rich in Cr (38 at %), and weak in Zr (01 at %) of the stainless steel side, we notice that Cr quickly decreases, for the benefit of increase in Zr (zone II) reaching a value of (38 at %). This report is in agreement with work of [12] on the sudden reduction in Cr, at the profit of Zr, Ni and Fe. Ni diffuses with Fe far in the interface reaching a distance from 110 μm approximately. It dissolves initially in the solid solution (αFeCr) of zone I, and then, it is found in the majority compound of zone III, with a concentration going from 5 to 8% of its weight.

Table 2: Quantitative analysis of the zones formed in the zone of diffusion between 304L and Zr4y, welded at 1020°C. Nature of the observed phases and the values of HV microhardness.

| Zones | éléments | At% | W% | Formed phases | Average of hardneses HV |
|-------|----------|-----|----|---------------|------------------------|
| (I) Edge of dark contrast | Zr | 1.14 | 1.90 | (α-FeCr) | 700 |
|       | Cr | 38.47 | 36.49 | | |
|       | Fe | 58.51 | 59.61 | | |
|       | Ni | 1.88 | 2.01 | | |
| (II) Gray pigmented | Zr | 37.52 | 50.26 | Zr(Cr-Fe)2 | 1400 |
|       | Cr | 26.83 | 20.49 | | |
|       | Fe | 35.33 | 28.98 | | |
|       | Ni | 0.31 | 0.27 | | |
| (III) Grise clear | Zr | 58.99 | 69.90 | Zr2(Fe1-xNiX), 0.15 ≤ x ≤ 0.25 | 850-610 |
|       | Cr | - | - | | |
|       | Fe | 31.65 | 22.96 | | |
|       | Ni | 09.36 | 07.14 | | |

3. 3. Nature of the phases formed at the interface

The chemical composition of zone I (table 2) gives a strong concentration of Fe(58.5%at.) and Cr(38.5 at %) and impoverished of Ni(1 at%) and Zr(2 at%). According to the diagram of balance of the elements majority Fe-Cr, he acts of the solid solution of αFe Cr type [16].

The specific chemical analysis in large particles of the pigmented phase of zone II (figure 1a) gives an atomic concentration of Zr(37.52 at %) Cr(26.83 at %) Fe(35.33 at %) and a very low Ni (0.31 at%) content, of the welded couple at 1020°C. That corresponds to the phase Zr(Fe, Cr)2 which has been also mentioned in certain work [17]. Zone II is consisted of Zr(Fe, Cr)2 majority, in the form of pigmented grains, coated in a matrix with αZr.

Zone III thickness of an approximate 60 μm for the welded couple at 1020°C consists of two phases. The first is the solid solution α Zr of Zircaloy4. The second phase in the shape of gray tablecloth, gives an average chemical composition of: Zr(58.99at%) Fe(31.65(at%)) and Ni(9.36(at%)) which corresponds to the phase Zr2(Fe1-x, NiX), where the solubility of Ni varies between 4.99 at% and 8.33 at%.

This compound which is located at Zy4 side, is formed thanks to the deep diffusion of Fe and Ni through the interface coming from steel before the formation of αFeCr and Zr(Fe, Cr)2 of steel side. This result is in conformity with work of [11] which also highlighted the formation of this compound. In the interface we have characterized no ternary compound between the elements Zr-Fe-Ni like it was proposed by certain authors in other work [4, 12].

The two-phase eutectic reactions βZr - Zr2Ni and βZr - Zr2Fe expected in the binary systems Zr-Ni [18] and Zr-Fe [16] of the Zr rich side, respectively at temperature of 1010°C, 960°C and 928°C are low, compared with those expected in the system Cr-Zr of the type βZr-ZrCr2 at T=1370°C [19]. The concentration of Fe is very high, compared with that of Zr in the junction of steel side. Consequently, the formation of these eutectics is improbable.
In front of the smoothness of the phases, constituent the various zones that we have characterized by MEB-EDS, we complete the work by the study in x-rays diffraction (DRX) aiming at, on the one hand, the confirmation or the cancel the results obtained and on the other hand, the determination others possible finer compounds, that have not been detected by the preceding technique.

The DRX spectrum of the junction Zy4/304L, welded at 1020°C which is given in figure 2. It presents multiple lines well formed with variable intensities. The results resulting from the x-rays diffraction with those available in literature, of diffusion bonding [11] and the TIG [4] obtained between the stainless steel (304L) and Zirconium alloys (Zy2 and Zy4) as well as the values drawn from JCPDS cards are deferred for comparison on table 3.

The results of certain authors [4, 11] indicate, the presence of the $\alpha$Zr solid solution, of the binary compounds: Zr$_2$Fe, Zr(Cr, Fe)$_2$, NiZr$_2$ and of the ternary compound X containing the elements Zr–Fe–Ni, to the interface. In our work, we have in addition to the binary phases quoted above; the presence of the phases ZrFe$_2$ ZrCr$_2$ and one $\alpha$FeCr solid solution. The light variation of the measured values of $d_{hkl}$ with those of literature can be allotted to the variation of the concentration of various elements of two welded materials.

Our results of XRD represented on table 3 and the spectrum of figure 2, are in good agreement with those obtained by (MEB - EDS). We have not analyzed of ternary compound Zr-Fe-Ni advanced by other authors [11, 12].

Moreover, in work of [13] on the elaboration of Zr-Fe-Ni system alloys, it is advanced that no ternary compound is formed in this system. We are in agreement with this work.

The binary compounds Zr$_2$Ni and Zr$_2$Fe, detected by DRX were not observed by MEB-EDS. They can be very fine and well localized in the interface also. They are, at the base of the formation of the compound Zr$_2$(Fe$_{1-x}$Ni$_x$) observed with MEB. Moreover, the two compounds Zr$_2$Ni and Zr$_2$Fe are mutually soluble and by diffusion of the chemical elements, they achieve the formation of the compound Zr$_2$(Fe$_{1-x}$Ni$_x$). This result is in good conformity with work of [7]. The interreticular distance ($d_{hkl}$ = 1.3697 Å) which corresponds for our work to the ZrFe$_2$ compound, could correspond to the compound of Zr(Cr-Fe)$_2$, as it is predicted [7] in its search. In addition, this value of ($d_{hkl}$ = 1.369 Å) is very close of those obtained by [4] ($d_{hkl}$ = 1.365 Å), this last specifies that it is in conformity with the phase of Zr(Cr-Fe)$_2$ type (table. 3). From these results we can affirm that the results obtained by MEB-EDS coincide perfectly with those obtained by x-rays diffractions.
Table 3: Results of the rays X (DRX) diffraction of the bonded couple at 1020°C between Zy4 and stainless steel.

| \(d_{hkl}\) (Å) | \(d_{hkl}\) (Å) | Identification (N° of JCPDS*) | hkl | [20] | \(d_{hkl}\) (Å) | \(d_{hkl}\) (Å) | \(d_{hkl}\) (Å) | Identification | hkl |
|-----------------|-----------------|-------------------------------|-----|------|----------------|----------------|----------------|----------------|-----|
| 2.8033          | 2.800           | ZrFe (25-420)                | 002 | 31.89| 2.799         | 2.79           | 2.800          | ZrFe          | 002 |
| 2.5779          | 2.573           | \(\alpha\)-Zr (5-0665)       | 002 | 34.77| 2.583         | 2.577          | (2.58)         | \(\alpha\)-Zr   | 211 |
| 2.4628          | 2.459           | ZrFe (26-809)                | 101 | 36.45| 2.463         | 2.457          | 2.459          | Zr-Fe-Ni      | 101 |
| 2.0766          | 2.070           | ZrFe (26-809)                | 202 | 43.66| 2.072         | 2.052          | 2.046          | ZrFe          | 310 |
| 1.8968          | 1.877           | ZrFe (5-0708)                | 231 | 48.04| 1.894         | 1.886          | (1.894)        | Zr-Fe-Ni      | 102 |
| 1.8023          | 1.830           | FeCr (5-0708)                | 222 | 50.73| 1.794         | 1.773          | (1.772)        | Zr-Fe-Ni      | 222 |
| 1.6163          | 1.616           | ZrFe (5-0665)                | 110 | 56.92| 1.612         | 1.613          | 1.616          | \(\alpha\)-Zr   | 110 |
| 1.4648          | 1.44            | ZrFe (18-666)                | 422 | 63.58| 1.458         | 1.461          | 1.463          | \(\alpha\)-Zr   | 103 |
| 1.3697          | 1.346           | ZrFe (18-666)                | 511 | 68.63| (1.365)       |                |                | Zr(Cr, Fe)2   | 302 |
| 1.3507          | 1.346           | ZrFe (18-666)                | 511 | 69.53| (1.346)       |                |                | ZrNi          | 322 |
| 1.2713          | 1.274           | ZrFe (5-0708)                | 422 | 74.58| (1.267)       |                |                | Zr(Cr, Fe)2   | 220 |
| 1.2264          | 1.218           | ZrFe (6-0612)                | 422 | 77.82| (1.174)       |                |                | ZrNi          | 521 |
| 1.1664          | 1.159           | ZrFe (25-420)                | 422 | 82.54| (1.179)       |                |                | ZrNi          | 114 |
| 1.1430          | 1.143           | ZrFe (25-420)                | 422 | 84.66| (1.174)       |                |                | ZrNi          | 521 |

\(0_{hkl}\): Measured values of this present study
\(1_{hkl}\): Indexed values of JCPDS cards of this work
\(2_{hkl}\): Values obtained by [4] from the zone of diffusion of welding by TIG between Zy4 and 304L
\(3_{hkl}\): Values obtained by [11] from the zone of diffusion of the zircaloy-2 side
\(4_{hkl}\): Values drawn from ASTM cards. \(4_{hkl}\) between brackets were indexed on the base of a tetragonal centered faces, with a = 6.51 Å and c = 5.54 Å by [11].

4. Microhardness of the welded couple

The values of the microhardness to the interface of the couple of materials, welded by diffusion (figure 1c), indicate that hardness is higher than those of the two basic materials to be assembled (stainless steel and Zy4) which give average microhardnesses oscillating between 200 and 250HV. These values increase in zone I of the solid solution (\(\alpha\)FeCr), rich in Cr (40%).

This element hardened the basic solid solution (\(\alpha\) Fe). The values of the hardness of the phase \(\alpha\)FeCr (fig.1c, zone I) correspond on average to 700HV, are in concord with the microhardnesses of the \(\alpha\)FeCr solid solution work of [20] on the development by thermal projection of FeCr on a carbon steel substrate.

In zone III, in the presence of the Zr(Fe1-xNi)x compound, the hardness decreases reaching the value of 613HV, which is approximately more than the twice those of stainless steel.

The microhardness of the phase of the Zr(Fe1-xNi)x type is at average of (1370HV), approach the values obtained on the same phase in work [5] on the welding between Zy4 and the stainless steel. This value is highest in the junction. The value of the hardness of the Zr(Fe1-xNi)x phase of zone III, varies between 850 and 613HV. This variation of hardness of the Zr(Fe1-x Ni)x phase is allotted to the variation of the solubility of Ni in this compound.
5. Conclusion

Diffusion bonding in a solid state forming a heterogeneous junction between stainless steel 304L and Zr-4 was carried out at the temperatures 850°C, 950 and 1020°C for one duration 45 minutes and under a dynamic pressure. The interface of diffusion widens according to the temperature. The distribution of the constitutive chemical elements through the interface between stainless steel and Zr4 was studied. The nature of the intermetallic compounds formed is determined by the combination of techniques of fine observation and chemical analyses and radio crystallographic. These compounds are of type Zr(Fe, Cr)12 Zr2(Fe1-xNiX), 0.15 ≤ X ≤ 0.25 and the solid solution αFeCr. These phases are located in the three following zones:

A zone of the stainless steel side, which is a solid solution αFeCr, representing an edging, rich in chromium, used as diffusion barrier of Zr. Its average hardness is 700HV.

An area (zone II) adjacent with the edge which was not previously mentioned, and which is composed mainly of an intermetallic compound of the type Zr(Fe, Cr)2 formed of faceted crystals of various dimensions. Its hardness is the highest. It culminates on average of 1370HV.

A third zone, side of Zr4 alloy made up of the solid solution αZr and, intermetallic compound of Zr2(Fe1-xNiX) type where X lies between 0.15 and 0.25. Its hardness varies between 613 and 850 HV.

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