RELIABILITY OF COMPUTER SIMULATIONS FOR THE DESIGN OF A COST EFFECTIVE LOW NI HEAT RESISTANT AUSTENITIC STEEL

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Abstract
The request from chemical industry for new cost effective with enhanced high temperature properties, has been more demanding. Computer analysis of phase relations and phase equilibria in multicomponent systems are increasingly used as a basis for alloy design of new alloys. Compositions can be identified which may be of a practical interest thereby reducing the amount of experimental work required to develop new and improved alloy. The reliability of thermodynamic databases used in the software THERMOCALC is important to give accurate prediction of the equilibrium fractions and compositions of the phases, critical transformation temperatures, element partitioning. In this work Thermocalc calculations was performed to identify a limited matrix of compositions, based on the analysis of equilibrium fraction and composition of the phases. The experimental work has been carried on six new compositions in comparison with two reference materials. The calculations resulted very valuable, although some limitations related to the use of a not fully reliable database has been found. One of the investigated alloys results to have a very good mechanical and creep behaviour and high resistance to relaxation cracking. The low ductility after ageing at room temperature has to be attributed to the large sigma phase fraction, not accurately predicted from modelling.

Introduction

In the chemical process industry the need to enhance the process conditions, both in terms of pressures and temperatures, in combination with a reduction of costs, represents the continuous driving force for the development of alternative higher strength materials. Another important factor to be considered is also the susceptibility to relaxation cracking after manufacturing processes [1]. All the existing materials have their limits in maximum design temperature or creep strength and only a few materials can be generally used at operating temperatures between 550 and 950°C. To date Alloy 800H results more favourable, because it can be used in a wide temperature range and its availability in many production forms and dimensions. However, due to the high Ni content (32 %) the Alloy 800H material is relatively expensive. Moreover, its creep strength is too low for new designs and highly susceptible for relaxation cracking after manufacturing processes.
Actually the alternative materials are available for lower temperature range. Particularly three steels have been developed: 1.4910, HR3C and NF709. The material 1.4910 (17Cr-13N-2.5M0), developed in Europe, has a significant lower Ni content than Alloy 800H (13 versus 32%). It is micro-alloyed with B and N, while the carbon content is strongly reduced. This material is not susceptible to relaxation cracking. The alloy HR3C (25Cr-20Ni) steel has been developed in Japan and it is micro-alloyed with N and Nb. The relaxation behaviour of this material is unknown up till now.

The objective of this paper is to describe the work performed to develop a new cost effective Fe base austenitic steel, with increased creep properties in a large temperature range: the target

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10^5hours creep rupture strength of the new steel is shown in fig.1, in comparison with the behaviour of some existing material, as a functions of the operating temperature.

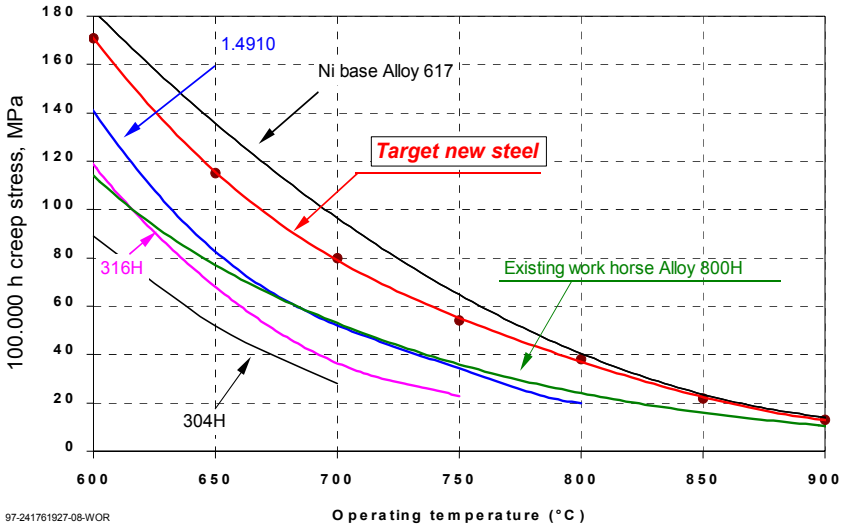

Fig. 1: 10^5h creep rupture strength new austenitic steel (target) compared to existing materials.

It is well known that the development of new alloys involves much work and a large experimental matrix. Computer analysis of phase relations and phase equilibriua in multicomponent systems are increasingly being used as a basis for alloy design, both for new alloys and for making improvements of existing alloy systems [2-3]. Compositions can thus be identified which may be of a practical interest thereby reducing the amount of experimental work required to develop new and improved alloy. The reliability of thermodynamic databases used in the software THERMOCALC is important to give accurate prediction of the structure stability, equilibrium fraction and compositions of the phases, critical transformation temperatures, element partitioning.
The chemical composition of the European material 1.4910 material has been the starting point for the development of the new austenitic steel for chemical industry.

1. Thermodynamic modelling

In order to develop a new heat resistant stainless steel the following metallurgical design criteria have been established [4]:

- **low amount of fine matrix carbides:** they have a detrimental effect on relaxation cracking susceptibility.
- **low amount of intermetallics**: they reduce the long-term solution hardening effect of the austenite and the room temperature ductility.
- **high amount** of **interstitial N** and **B** in the austenite: these elements are very effective to increase creep strength and stability of the austenite. Moreover, interstitials seem to reduce the relaxation cracking susceptibility of austenitic materials.
- **No δ- ferrite**, that decreases ductility**.**

THERMOCALC analysis has been carried out on several compositions based on 1.4910 and HR3C materials by using the SSOL database. The calculations on reference materials have been also performed to assess the databases. For these materials some inaccuracies especially for alloys with a very high Ni content have been found.
Furthermore, the modelling results can be considered as a guideline, especially with regard to the precipitation of (undesirable) intermetallic phases (Sigma, Laves). The long-term effect of solution hardening elements cannot be evaluated by equilibrium calculations, especially regarding the effect

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of the interstitial Nitrogen and Boron that are fixed in nitrides and borides after long times. For example the calculations predict borides formation at very high temperatures, as stable phase with a very low amount of B in the austenite matrix. On the contrary, the existing practical experiences give indication that boron solubility is generally higher than the predicted values [4].
A matrix of eighteen compositions based on 1.4910 reference material and four on HR3C steel, have been evaluated by Thermocalc. The alloying elements have been varied as follows:

- $0.02 < C < 0.01$
- $16 < Cr < 20$
- $13 < Ni < 17$
- $0 < Mo < 2$
- $0.15 < N < 0.35$

Also the effect of Ti, Nb and V additions has been evaluated. The calculations have been performed also suspending second phases to simulate the conditions of the materials before starting the service. For all the compositions critical temperatures and phase fractions as a function of temperature have been calculated. Boron has been not considered in the calculations since its presence gives some troubles in determining the solidus temperature.
By analysing the results obtained from these preliminary calculations five promising chemical compositions were defined as presented in Table I: four compositions are based on 1.4910 material and one on HR3C material.

Table I: Chemical composition (wt%) of the first 5 selected experimental alloys and the 2 reference materials.

Alloy	C	Mn	Si	Cr	Ni	Mo	Al	Fe	N	B	Nb	V
reference 1.4910	.02	1.5	0.50	17	13	2.5	--	bal	0.14	0.004	--	--
1	.02	1.5	0.50	20	14	2.5	--	bal	0.25	0.004	---	---
2	.02	1.5	0.50	20	12	---	--	bal	0.25	0.004	---	---
4	.02	1.5	0.50	20	15	2.5	-	bal	0.25	0.004	---	.30
5	.08	1.5	0.50	20	12	2.5	--	bal	0.25	0.004	--	---
reference HR3C	.08	1.5	0.50	25	20	---	---	bal	0.25	---	0.40	--
6	.02	1.5	0.50	26	17	---	---	bal	0.35	0.004	--	---

The results of phase fractions calculations, as function of the temperature for the selected compositions are summarised in Table II.

Table II : Summary of Thermocalc results for critical transformation and precipitation temperatures

Alloy	T_{liq}	T_{sol}	$T_{M(C,N)}$	T_{Cr2N}	T_{M23C6}	T_{Sigma}
reference heat 1.4910	**1413**	**1369**	**--**	**--**	**877**	**629**
1: 14910 variant	1396	1341	--	1033	886	722
2; 14910 variant	1415	1370	--	769	811	639
4; 14910 variant	1393	1341	1226	1090	821	735
5; 14910 variant	1394	1327	--	1038	1010	689
reference heat HR3C	**1380**	**1303**	**1332**	**--**	**1031**	**663**
6; HR3C variant	1383	1318	--	1012	866	724

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The total amount of carbides/carbonitrides for the selected alloys is not too much higher than the reference alloys except for the compositions with the highest C and N respectively (fig. 2). In particular the alloy 4 is characterised by a high content of vanadium carbides that are generally considered positive to increase creep strength. The precipitation of intermetallic phases starts at atemperature generally lower than 700°C (fig.3). With decreasing temperature their fraction increases rapidly**.** Anyway the times to reach equilibrium phase fractions becomes longer as the temperatures are decreased.

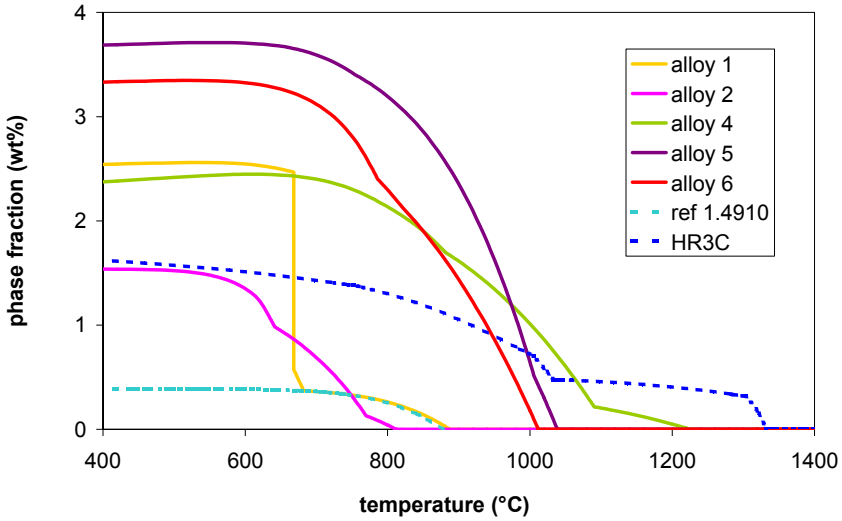

Fig. 2: Calculated equilibrium fraction of carbides and carbonitrides as function of temperature

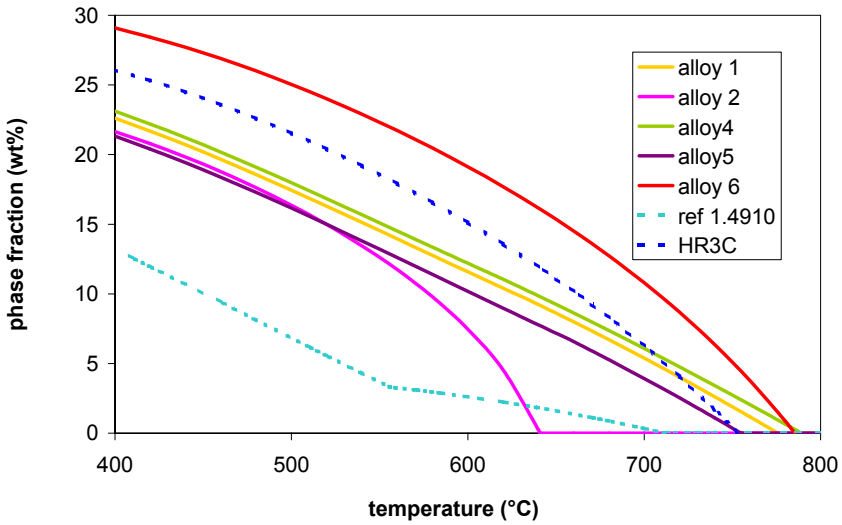

Fig. 3: Calculated equilibrium fraction of intermetallics phases as function of temperature

The solubility of nitrogen in the austenitic matrix is very low at the equilibrium state (fig.4), similarly to that of Mo. Anyway, these elements are fixed in nitrides and intermetallic phases respectively, with unknown kinetic rates, which depend inversely from the temperature.

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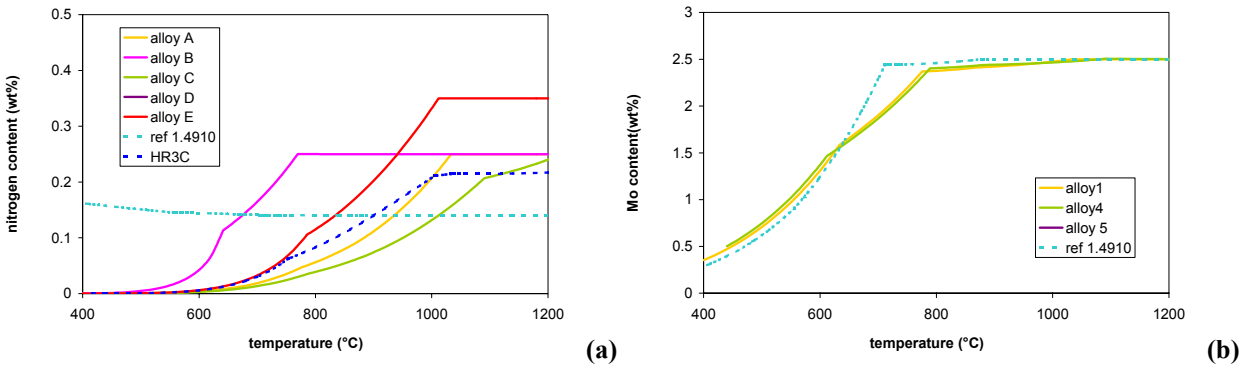

Fig. 4: Calculated equilibrium nitrogen (a) and molybdenum (b)content in the austenitic matrix phases as function of temperature

2. Experimental procedures

Based on the calculations, five laboratory and two reference materials heats have been produced for the assessment of the standard mechanical properties and short term high temperature stability. The chemical analysis of the produced ingots are reported in table III. The ingots have been hot rolled and the obtained plates have been heat treated at 1200°C for two hours.

Tensile tests from room temperature to 850°C have been performed. Charpy V tests have been carried out on hot rolled and heat treated plates and after further ageing at 650°C, 750°C and 850°C up to 1000 hours. Isostress creep tests at 3 stress levels (77MPa, 36MPa and 16MPa) have been conducted. In order to establish the sensitivity for in service Relaxation/Stress Induced Cracking a three point bend test has been used (with an equipment and procedure developed by TNO). Before the tests the specimens have been cold deformed up to 15%: relaxation times up to 150 hours and temperature of 600°C and 650°C have been used. The assessment of damage has been performed on cross section specimens by metallographic analysis. The damage is classified in 4 categories:

- Class 0: no damage. Material not susceptible for relaxation cracking.
- Class 1: cavities. Material not susceptible for relaxation cracking.
- Class 2: microcracks and cavities. Material susceptible for relaxation cracking.
- Class 3: macro/microcrack, cavities. Material very susceptible for relaxation cracking.

Microstructure analysis by SEM equipped with EDX spectometer, have been performed on as delivered and aged materials.

Table III: Chemical composition of the laboratory experimental heats

Alloy	C	Mn	Si	Cr	Ni	Mo	N	B	V
1	0.019	1.474	0.495	20.23	14.17	2.48	0.277	0.0038	--
2	0.020	1.511	0.493	19.96	11.95	--	0.276	0.0033	--
4	0.019	1.495	0.507	20.07	14.82	2.511	0.264	0.0047	0.303
5	0.072	1.468	0.501	20.08	12.13	2.518	0.267	0.0044	--
6	0.022	1.499	0.513	25.9	17.32	--	0.351	0.0037	--
reference Alloy 800	0.022	1.499	0.513	25.94	17.32	--	0.351	0.0037	--
reference 1.4910	0.072	1.468	0.501	20.08	12.13	2.518	0.267	0.0044	--

3. Results

The tensile strength of the laboratory heats are generally higher than that of reference materials (fig. 5): the addition of V results in an extra increase of tensile properties (alloy 4), while the absence of Mo (heat 2) reduces UTS.

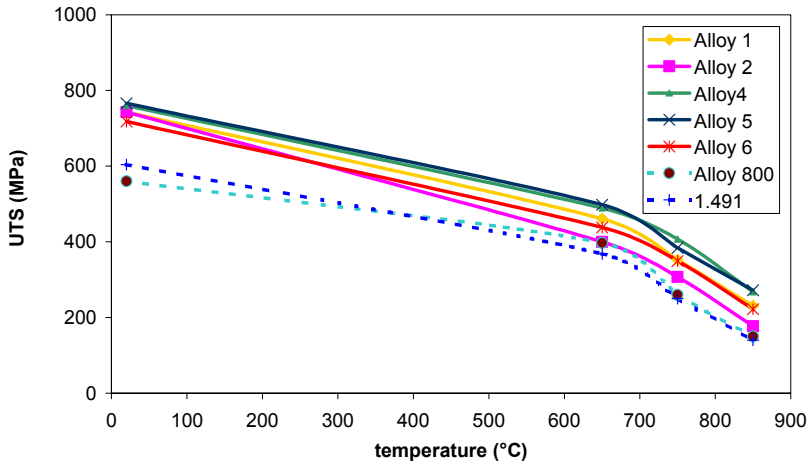

Fig. 5: Tensile strength of 5 laboratory heats and 2 reference materials

The results of toughness tests, presented in fig. 6 (reported as function of Larson Miller Parameter PLM), show for all the laboratory heats a strong drop in toughness. Only alloy 2 maintains high Charpy V energy values. The toughness of reference materials is significantly higher.

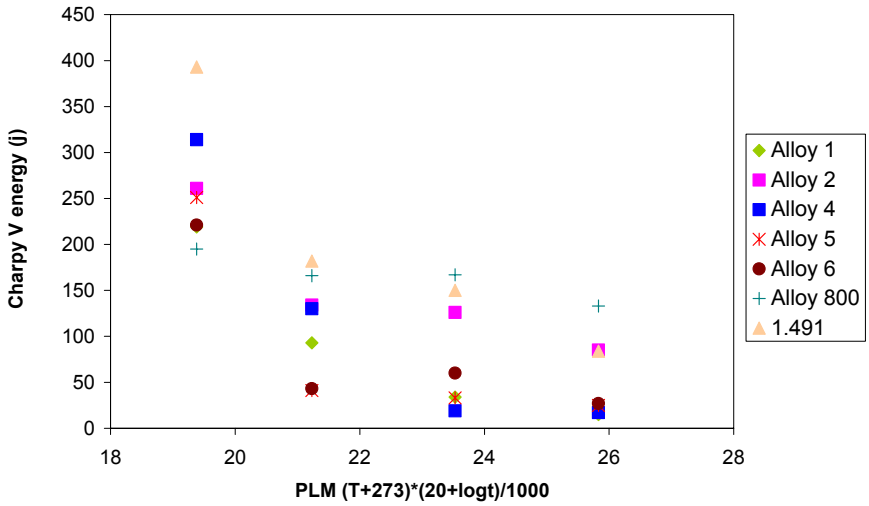

Fig. 6: Toughness of 5 laboratory heats and 2 reference materials

Results of creep tests are summarised in figure 7 that show the rupture time as function of temperature, for the used stress levels. The creep rupture lifetimes of alloy 2 are significantly lower than the lower bound of the scatterband of Alloy 800. alloys. The alloys 4, 5 and 6 show at 77 MPa rupture lifetimes close to the upper scatterband of Alloy 800 and always higher than that obtained form the second reference material. At 16MPa stress level the alloy 4 and 5 are comparable with the average values for alloy 800.

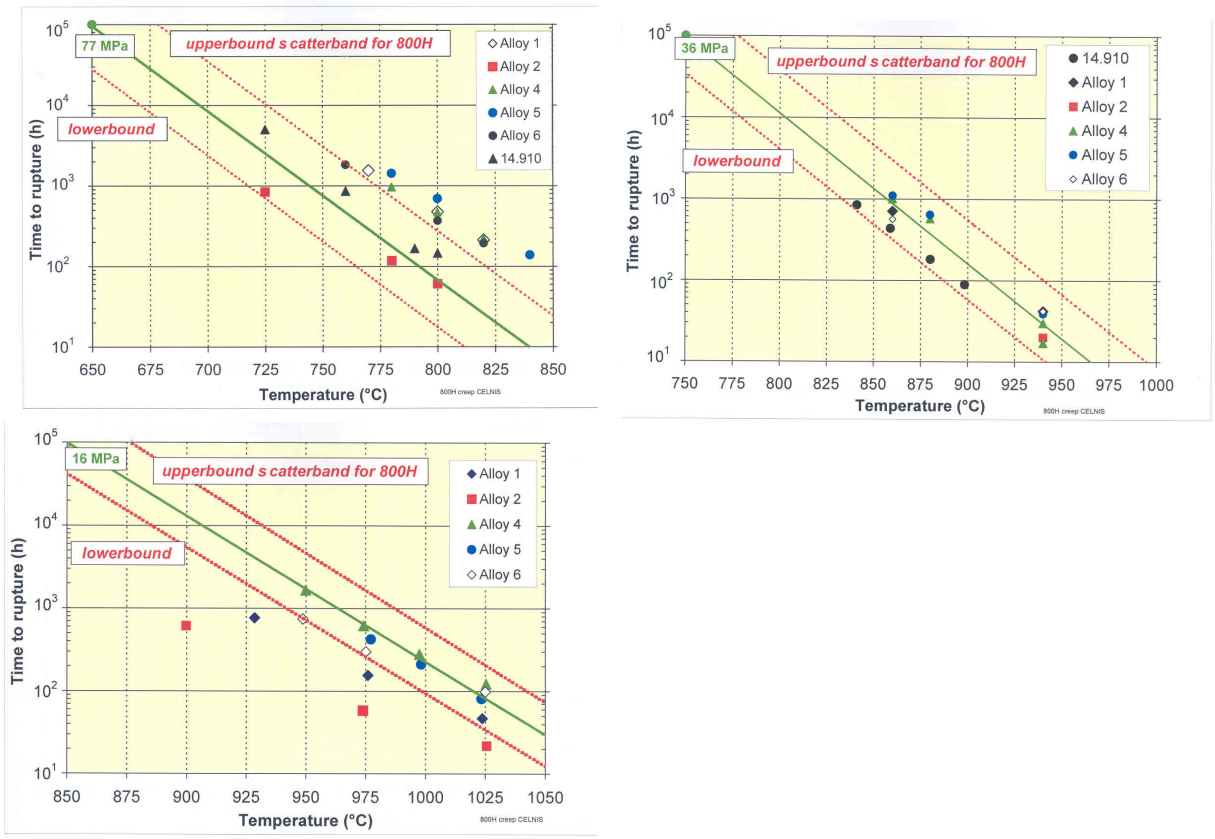

Fig. 7: Results of isostress creep tests with stress level of 77MPa, 36MPa and 16MPa

An overview of the results of the relaxation tests is given in table IV. The 1 and 4 alloys can be classified as not susceptible for relaxation. On the contrary, the alloy 2 is extremely susceptible, even more than the reference material Alloy 800.

Table IV: Summary of relaxation tests results

Alloy	650°C		650°C	
1	1	= some cavities	0	= macrocracks
2	3	= macrocracks	3	= macrocracks
4	1	= some cavities	0	= macrocracks
5	2	= microcracks	2	= macrocracks
6	3	= no damage	2	= macrocracks
Alloy 800	0	= macrocracks	--	= macrocracks
1.4910	3	= no damage	--	= macrocracks

The effect of ageing on the precipitation behaviour has been also analysed. The results of the phase counting performed on materials after ageing for 3000hours at 850°C, are summarised in table V. The carbonitrides are essentially a Cr rich phase (Cr> 80-90%) in all the alloys. Only the alloy 4 shows a fine precipitation of (Cr,V) nitride (fig. 8).

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Table V: Amount of secondary phases (%) after 3000 h ageing at 850°C

Alloy	Sigma	Carbo/nitride	$M_{23}C_6$
1	2.7	1.1	--
2	--	1.4	--
4	6.0	1.1	--
5	1.8	1.3	0.6
1	Traces	1.5	0.2
Alloy 800	1.5	--	Traces
1.4910	--	--	1.1

Table VI presents a summary of SEM observations performed to identify the phases present both at grain boundary and inside the grains on the alloy 4 and reference materials. The globular phases (1-10µm) mainly present at grain boundaries, have been identified as CrFe Sigma phase, but containing up to 12% Mo. The fine precipitation of Cr and V nitride has also been identified, both at grain boundaries and inside the grains. The 1.4910 reference material is characterised by the presence of sigma phase with higher content than that observed in alloy 4, although the Mo content is lower. It has been also found that some grain boundaries are marked by coarse $Cr_{23}C_6$ carbides. In alloy 800 only intergranular fine $Cr_{23}C_6$ have been detected.

Table VI: Chemical analysis of secondary phases by SEM/EDX after 3000 h ageing at 850°C

Alloy	Phase	Location	C	N	V	Cr	Fe	Ni	Mo
4	Sigma CrFe	Inter + Intra			0.2	30.6	46.6	6.7	12
	$(CrV)_2N$--			11	5.9	43.3	28.2	5.9	2.6
Alloy 800	Sigma MoFe	Inter + Intra				23.4	47.2	4.2	20.5
	$Cr_{23}C_6$	Inter	6.9			57.6	19.8	2.5	11.3
1.4910	$Cr_{23}C_6$	Inter	6.4			67.7	15.7	7.9	1.2

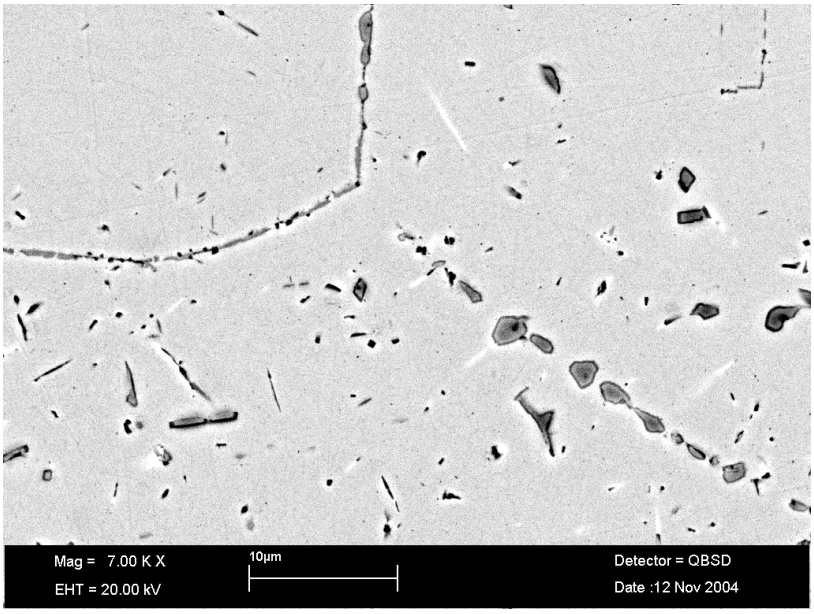

Fig. 8: Second phase distribution on the grain boundary and inside the grains of the alloy 4

4. Discussion

The use of thermodynamic modelling as support to the development of new materials allows to reduce the amount of experimental work, with consequent cost and time saving. In the frame of this work Thermocalc has been used to define a limited matrix of compositions for the experimental investigations. Preliminary calculations have been performed to investigate the combined effects of the alloying elements on the phase equilibria. The metallurgical criteria for the design of a new cost effective alloy for application in chemical industry are based on the need to reduce nickel addition. In order to control solidification, avoiding the presence of residual delta ferrite on the final product, Cr and other ferritising elements, such as Mo, have been carefully controlled. Furthermore Cr and Mo are key elements to induce respectively corrosion resistance and solid solution strengthening to the material. Nitrogen is also an important element to induce good mechanical properties, especially as interstitial element. Anyway, nitrogen tends to be fixed in chromium nitride, that is the stable phase, during the service at high temperature. Obviously a lower temperature of nitride (and carbide/carbonitride) formation reduces the precipitation rates. The same concept can be applied to intermetallic phases, which are particularly dangerous to reduce ductility and toughness of the steel. From the above considerations the need of tools to control the complex equilibria in such as multi-element alloys is evident. Obviously, Thermocalc modelling produces predictions that strictly apply only to equilibrium conditions. Anyway, some indications can be provided also on non equilibrium systems, by taking into account information on kinetics deriving from practical experience. For this reason calculations have been also performed by suspending the second phases, in order to simulate the system in the as delivered conditions, after the solubilization heat treatment at 1200°C.

The reliability of database is the key factor to obtain a good description of the phase equilibrium. The used database results not reliable particularly on the prediction of the temperature formation of intermetallic phases. As it has been observed from experimental analysis, sigma phase is present up to 850°C, temperature at which the coarsening rates are very high, compared to the estimated temperatures that were generally lower than 700°C. Similar discrepancies have been found also on predictions for 9Cr ferrritic steels [5], for which a specific database was developed [6]. The unexpected low toughness properties of the investigated compositions have been attributed to the high fractions of coarse sigma phase, developed during the ageing at high temperatures. Anyway, from the analysis of the experimental work the following considerations can be done:

- the increased nitrogen content (with respect to the reference alloys) produce a fine precipitation of carbonitrides that contribute to mechanical strengthening. The coarsening of this phase, especially at the higher temperatures, can reduce this effect, jointly with ductility.
- Mo absence avoids the formation of sigma phase thus maintaining a good level of toughness after ageing. Anyway the mechanical properties and creep strength result lower than those obtained on Mo alloyed compositions. Furthermore the Mo addition is necessary to guarantee resistance to relaxation cracking.
- V addition results in the precipitation of very fine carbo-nitrides in the matrix, suppressing precipitation at grain boundaries: this distribution strongly increases the mechanical properties and creep resistance.
- Carbon increase produces an increase of carbides fractions, especially of grain boundary $M_{23}C_6$. The creep resistance increases but the steel results extremely susceptible to relaxation cracking.

Even if not all the target requirements have been reached for the selection of the new alloy, important indications have been obtained from this work for further tuning of composition. On the basis of the present results the more promising alloys is the alloy 4, also if toughness after ageing is low. However many existing creep resistant materials show comparable ductility drop. Although room ductility temperature values are preferable, the high temperature ductility is more essential property.

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5. Conclusions

Thermodynamic modelling has been performed to support alloy design of new alloys for petrochemical applications with increased mechanical properties. However the success of thermodynamic modelling depends critically on the use of highly-quality validated databases.

Within the present work promising chemical compositions have been formulated by using support of Thermocalc analysis. Although the calculations resulted very valuable in guiding the selection of materials, it has to be in due consideration that the thermodynamic predictions always refer to equilibrium states that can sometimes differ significantly from the actual microstructures found in real long term treatments.

The success of the use of thermodynamic modelling depends critically on the use of high quality validated databases and experimental work to verify the reliability of calculations is demanding.

In this paper the main limitation on the use of thermodynamic calculations have been outlined, which are related to the need to verify the results against experimental information before conclusions can be drawn. Anyway, the results obtained on one of the investigated compositions appear very interesting and starting from this work further refinement in order to satisfy all the required properties is currently is in progress.

References

1) P.A. COLLINS, Z.A. FOROULIS and M.J. HUMPRIES, Int. Conf. on "Corrosion and Mechanical Stress at High Temperatures", Petten, The Netherlands 1980, p. 359.
2) N. SAUNDERS, P. MIODOWNIK, CALPHAD-A Comprehensive guide (New York, Elsevier Science, 1998)
3) B. JANSSON, M. SCHALIN, M. SELLEBY, B. SUNDAMAN, Computer Software in Chemical and Extractive Metallurgy , eds. C. W. Bale and J. A Irins, Canadian Inst. Met., (1993), p. 57
4) T. SOURMAIL, Mat.. Sc. Techn. 17, (2001), p.1
5) J. HALD, New Steels for Advanced Plant up to 620°C, London, May 1995, E. Metcalfe (ed.), EPRI, USA , 1995, p.. 152
6) J. HALD, L. KORCAKOVA, ISIJ Int. Vol. 43, (2003), p. 420

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