Metallurgical design of high-toughness, high-strength steels for 300 bar gas cylinders applications

A.Saccocci
P.E. Di Nunzio

RINA

Summary

Transportable cylinders for industrial gases with improved mechanical properties such as strength, toughness and fatigue resistance → lighter steel cylinders with higher strength levels.

Metallurgical design of quenched and tempered (Q&T) steels with Ultimate Tensile Strength (UTS) greater than 950 MPa and total elongation greater than 14%

Chemical composition due to industrial constraints, two types of steel grades have been developed and investigated → Cr-Mo and Cr-Mo with V micro-addition;

Literature, commercial and in-house metallurgical models have been used to identify the most suitable chemical compositions for laboratory heat productions following the typical industrial processing route → hot rolling of lab heats, oil quench & tempering undergo industrial conditions

Metallographic and mechanical characterizations → tensile strength higher than 950 Mpa; impact toughness higher than 50 J/cm^2

Introduction

- Aim of this work is to design a suitable chemical composition for a steel to produced Gas Cylinders (GC) starting from ***seamless pipe*** with improved mechanical properties (strength, toughness and fatigue resistance) to **reduce the total weight;**

- Lighter gas cylinder storage applications at a pressure up to 300 bar, compliant with the **EN 1964/2** (ISO 11114-4) standard → tensile strength **>950 MPa**, total elongation **>14%** and average impact toughness at **-50°C of 50 J/cm^2** with a minimum value not below **35 J/cm^2**

- Compared to the manufacturing process from seamless tube, the construction by pressing a flat plate/strip offers some advantages in weight reduction because the geometrical tolerances are usually better and the minimum required thickness can be achieved maintaining the maximum thickness to lower levels than those from seamless tubes;

- Typical vessels Outer Diameter **227÷229 mm** and thickness **6.8÷7.6 mm**. (The mechanical performance of the new steel grade must be able to compensate relatively large tolerances typical of seamless tube).

Metallurgical Design

Starting point current commercial composition for components, oil-quenched and tempered for 40 minutes at 600°C, are characterized by a just sufficient toughness level (55 to 60 J/cm^2 in the average) at -20°C.

Chemical composition (mass%) of commercial steels currently used for 300 bar cylinders.

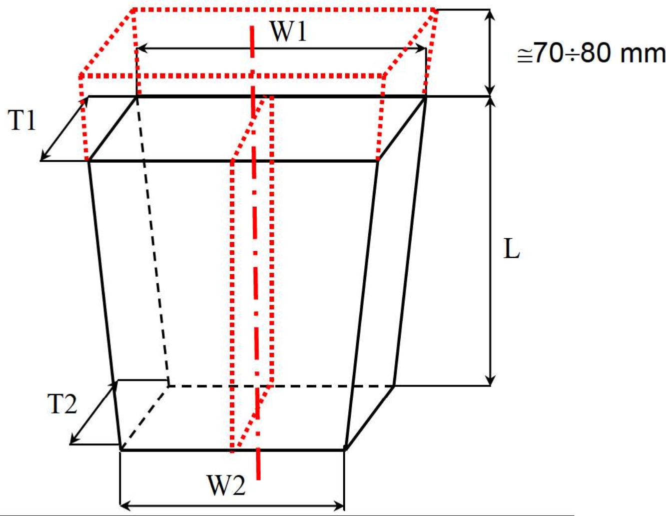
	C	Mn	Si	Ni	Cr	Mo	Al	V	N
Ref. 1	0.35	0.70	0.20	<0.15	1.0	0.22	0.030	<0.01	<0.011
Ref. 2	0.36	0.75	0.20	<0.15	1.0	0.40	0.030	<0.01	<0.011

Metallurgical Design

- Besides the chemical composition tempering temperature has been considered as a key parameter in the production process;
- Alloy design by using literature and in-house empirical models;
- Chemical Compositions (CC) with critical cooling rate to ensure fully martensitic structure using oil quenching
- CCs have been ranked on predicted hardness as a function of the tempering temperature in the range 550÷700°C for 40 minutes
- These compositions have been cast in laboratory, hot rolled, then oil quenching and finally tempered → **reproducing as close as possible the industrial route.**

Metallurgical Design

Vacuum Induction Melting Facility at CSM



Dimension of useful material casted at VIM

W1xT1xL (mm)	*W2xT2xL (mm)*	*Weight (kg)*
250x125x250	240x110x250	75

Metallurgical Design

Hot Rolling pilot plant at CSM

Roughing mill			
No pass	t *(mm)*	R.R. *(%)*	T *(°C)*
1	120	-	1250
2	95	21	-
3	70	26	-
4	49	30	-
5	35	29	-
6	25	29	
7	20	43	≥950
Total R.R.		83	

Dimension before roughing	
Small section	110x115 mm^2
Large section	120x120 mm^2
Lenght	320 mm
Sprue	100,110 mm
Weight	35 kg

Dimension after roughing
21x155x900 mm^3

Finishing mill			
No pass	t *(mm)*	RR *(%)*	T *(°C)*
1	14	30	1150
2	10	29	≥900
Total R.R.		50	

Dimension before finishing
21x155x300 mm^3

Dimension after finishing
11x165x600 mm^3

Roughing and finishing mill schedules.

Metallurgical Design

First chemical composition design

- GC1 → improve the **toughness**, **microstructure uniformity** avoid the formation of bainite after oil quenching (reducing C below 0.3% wt, reducing Mo below 0.3% wt, increase Cr above 1%)

- GC2 → **improve the strength (V micro-alloyed, increase Mn)**

	C	Mn	Si	Ni	Cr	Mo	Al	V	N
GC1	0.25	0.80	0.20	0.5	1.20	0.30	0.030	<0.005	0.0050
GC2	0.27	1.00	0.30	0.6	1.50	0.20	0.025	0.060	0.0075

Metallurgical Design

Second chemical composition design (optimization)

- GC3, GC4 → **Increase the Mn content up to 1.30% wt**
- GC3, GC4 → **to prefer Mo rather than Cr (hardenability, GC3 Cr 0.4% Mo 0.6%, GC4 Cr 0.56%, Mo 0.4%)**
- GC4 → **improve the strength (V micro-alloyed, increase Mn)**

	C	Mn	Si	Ni	Cr	Mo	Al	V	N
GC3	0.27	1.30	0.30	0.6	0.40	0.60	0.022	<0.005	0.0055
GC4	0.27	1.30	0.30	0.6	0.56	0.40	0.022	0.050	0.0055

Metallurgical Design

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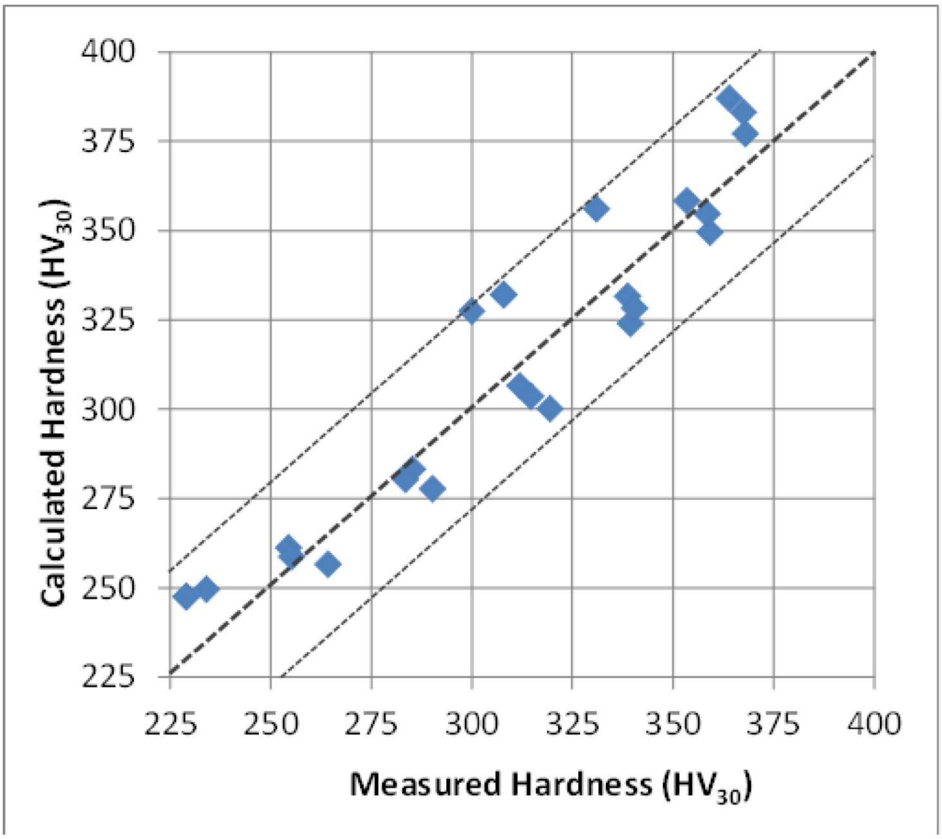
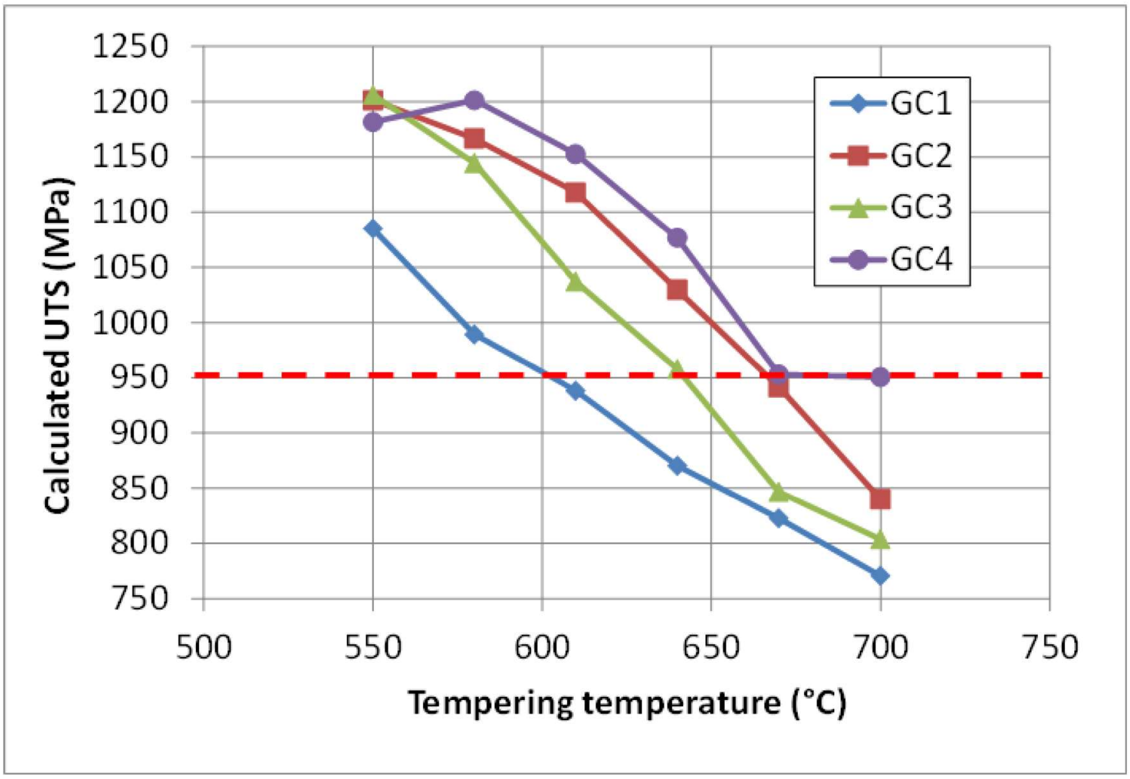
Metallurgical Design



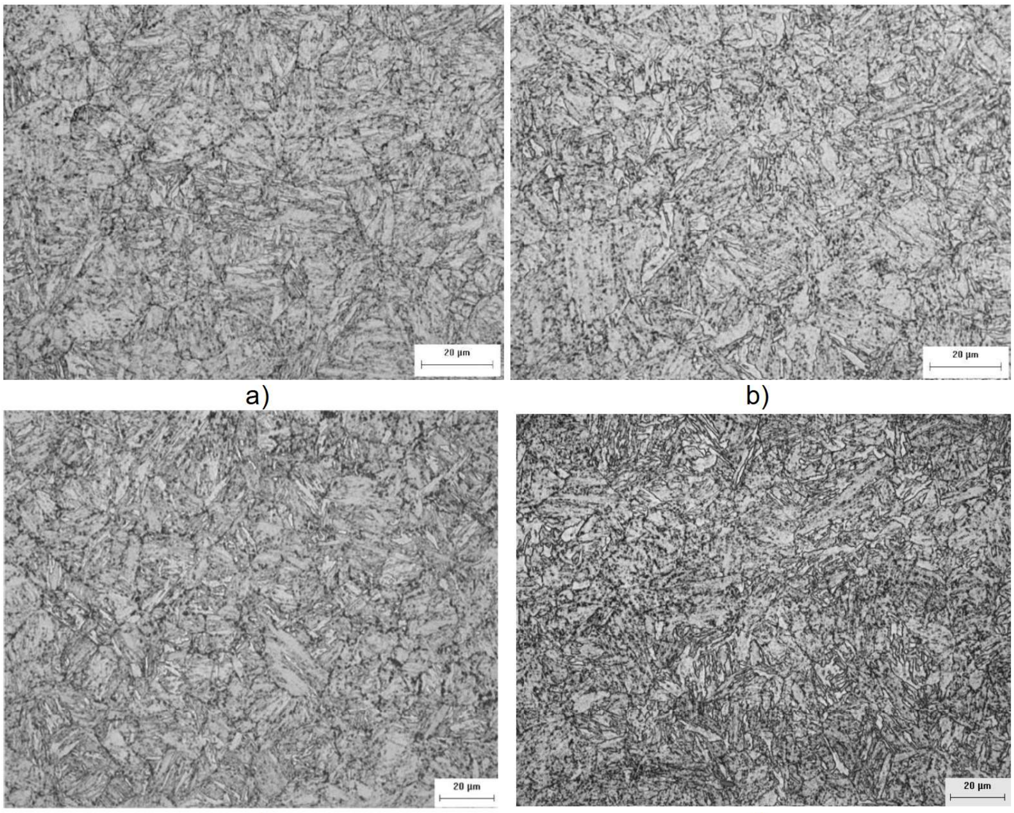
Performance prediction model for hardness after 40 min tempering in the range 700-550°C starting from a fully martensitic microstructure. The ±2 standard deviations confidence band is also reported.

Metallurgical Design



UTS as a function of the tempering temperature calculated from the estimated hardness. The horizontal dashed line is the minimum strength according to the reference standard for the component.

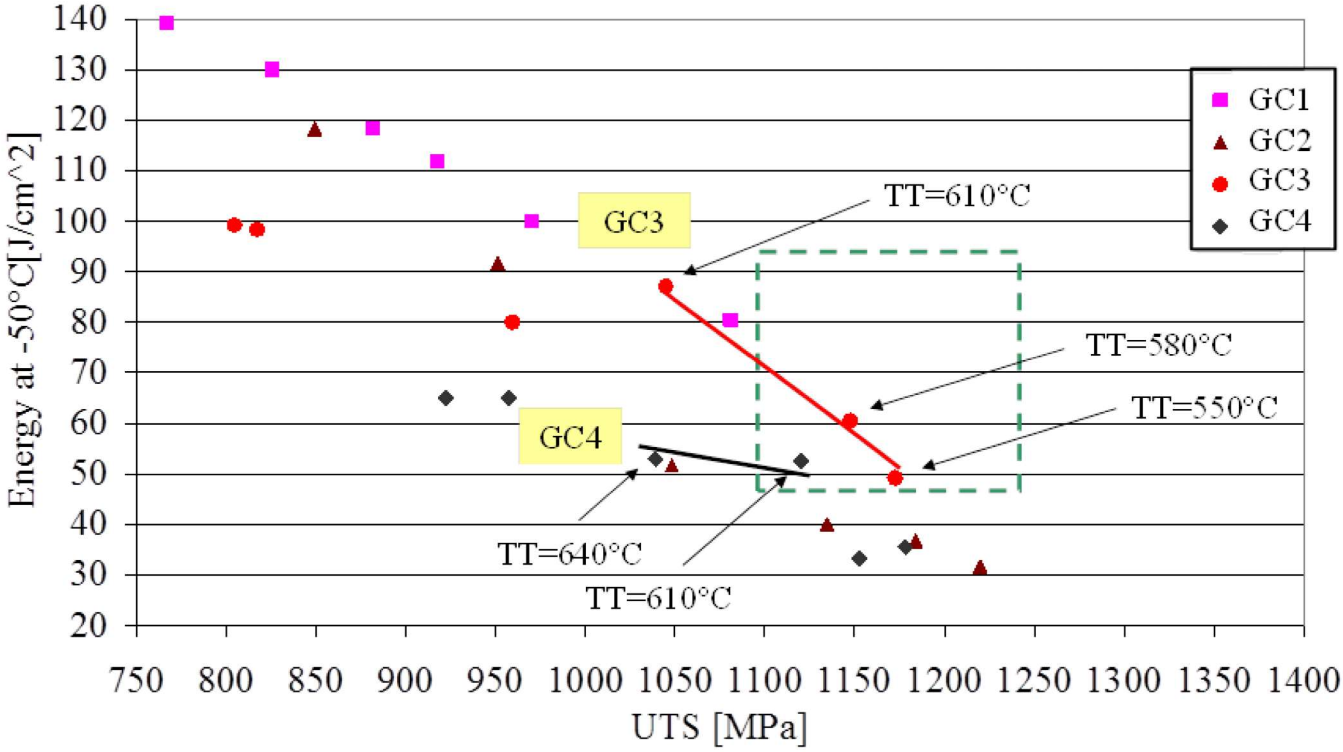
Metallurgical Design



a) b) c) d)

Fig. 3. Microstructure of the Q&T steels in transverse direction: a) GC1 tempered 40 min at 580°C; b) GC1 tempered 40 min at 580°C; c) GC2 tempered 40 min at 580°C; d) GC2 tempered 40 min at 700°C.

Optimization of the materials performance



Charpy V-notch impact test at -50°C on transversal specimens for all the steels and tempering treatments (TT) versus their respective measured UTS. The dashed box represents the acceptance region according to the reference standard for the component.

Optimization of the materials performance

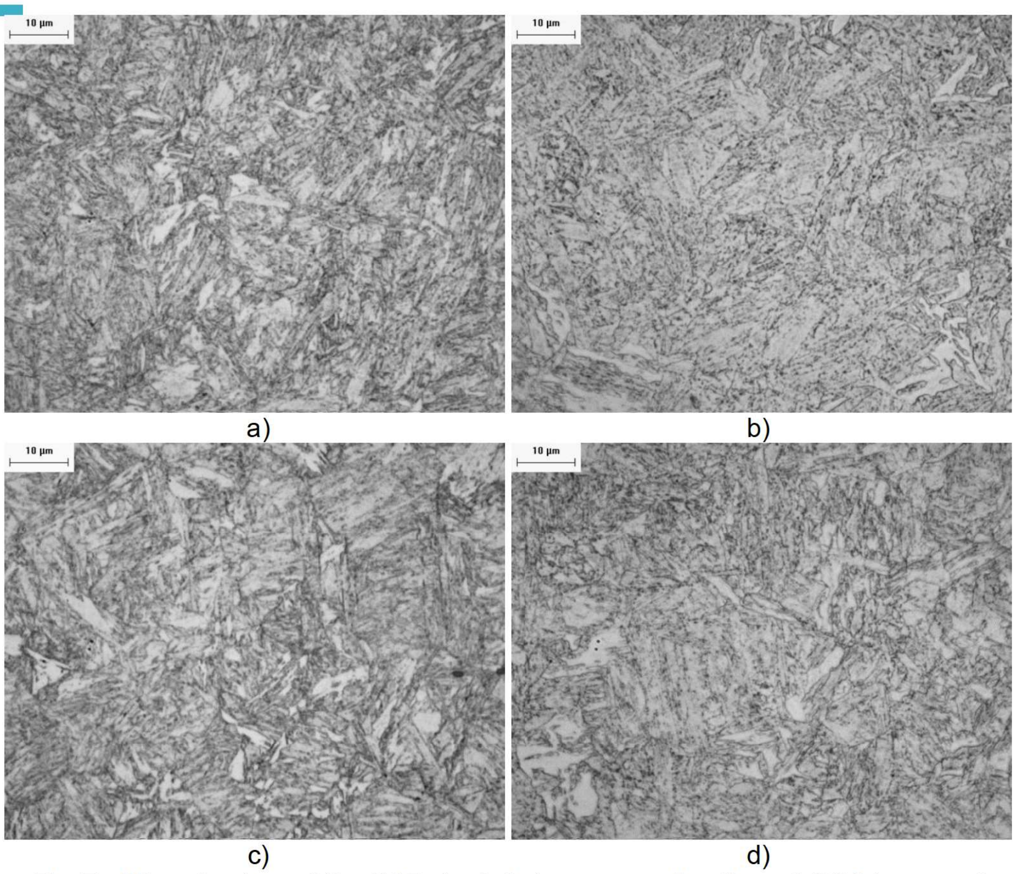
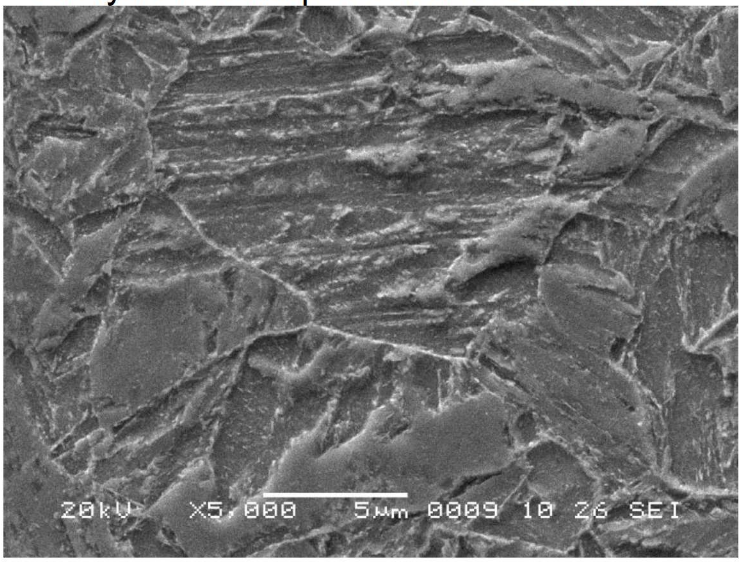


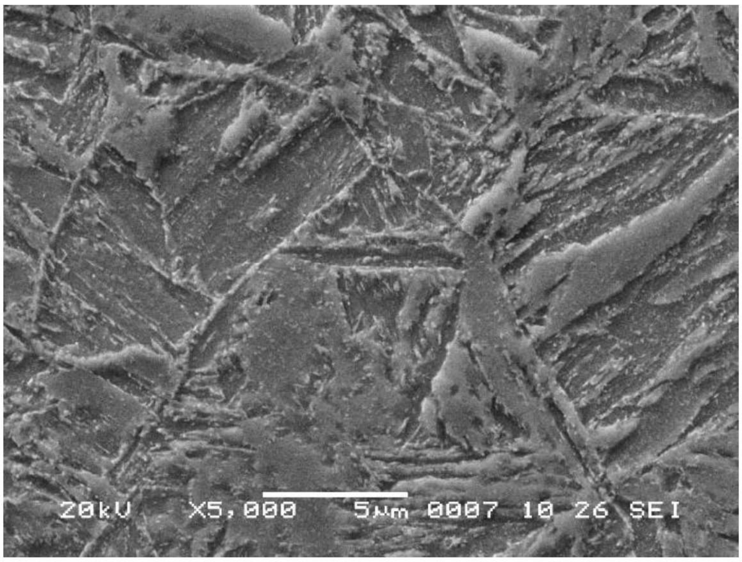
Fig. 7. Microstructure of the Q&T steels in transverse direction: a) GC3 tempered 40 min at 580°C; b) GC3 tempered 40 min at 700°C; c) GC4 tempered 40 min at 580°C; d) GC4 tempered 40 min at 700°C.

Optimization of the materials performance

- Two tempering conditions producing similar UTS are compared.
- Tempered martensite where precipitation of carbides along grain boundaries and within the martensite laths, especially in the V- added variant GC4.
- The extremely fine precipitation produced tempering is difficult to be characterized by micro-analytical techniques such as SEM-EDS.



a)



b)

Fig. 8. SEM images of the microstructure of the Q&T steels: a) GC3 tempered 40 min at 580°C; b) GC4 tempered 40 min at 610°C.

Optimization of the materials performance

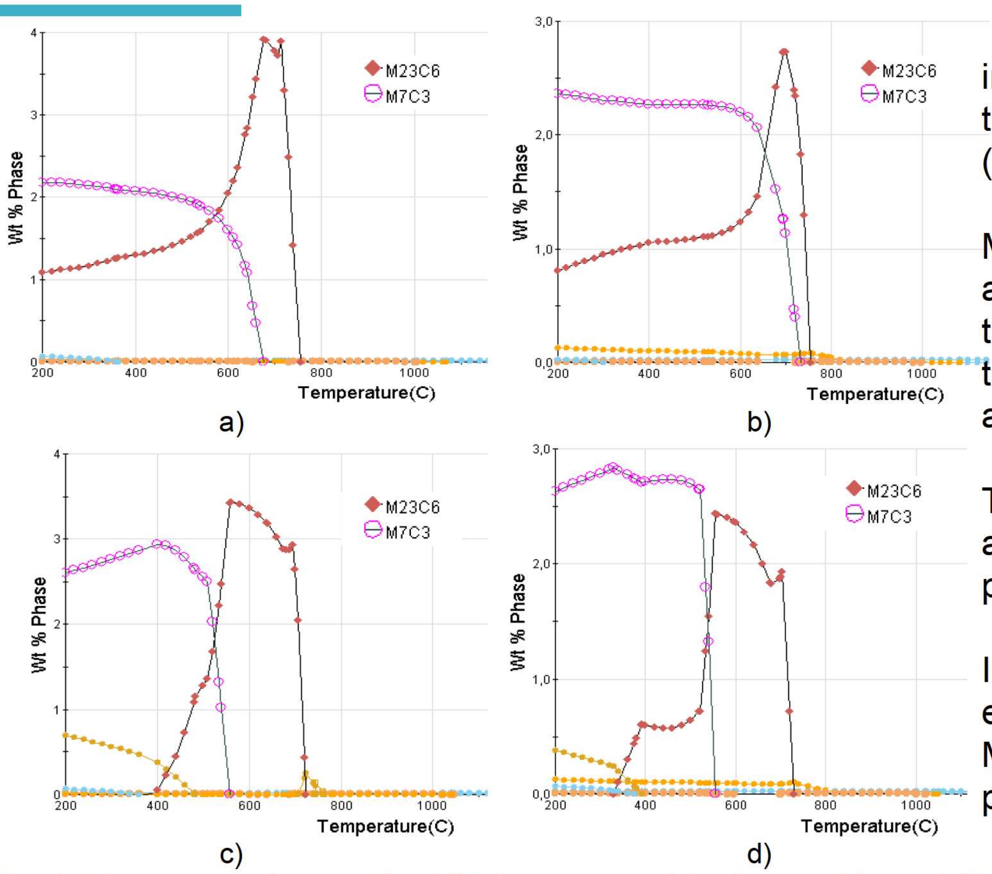


Fig. 9. Thermodynamic evaluation (JMatPro commercial software) of the stability ranges of precipitates formed after tempering in the range from 700 to 500°C: a) GC1; b) GC2; c) GC3; d) GC4.

investigation by commercial thermodynamic software (ThermoCalc and JMatPro)

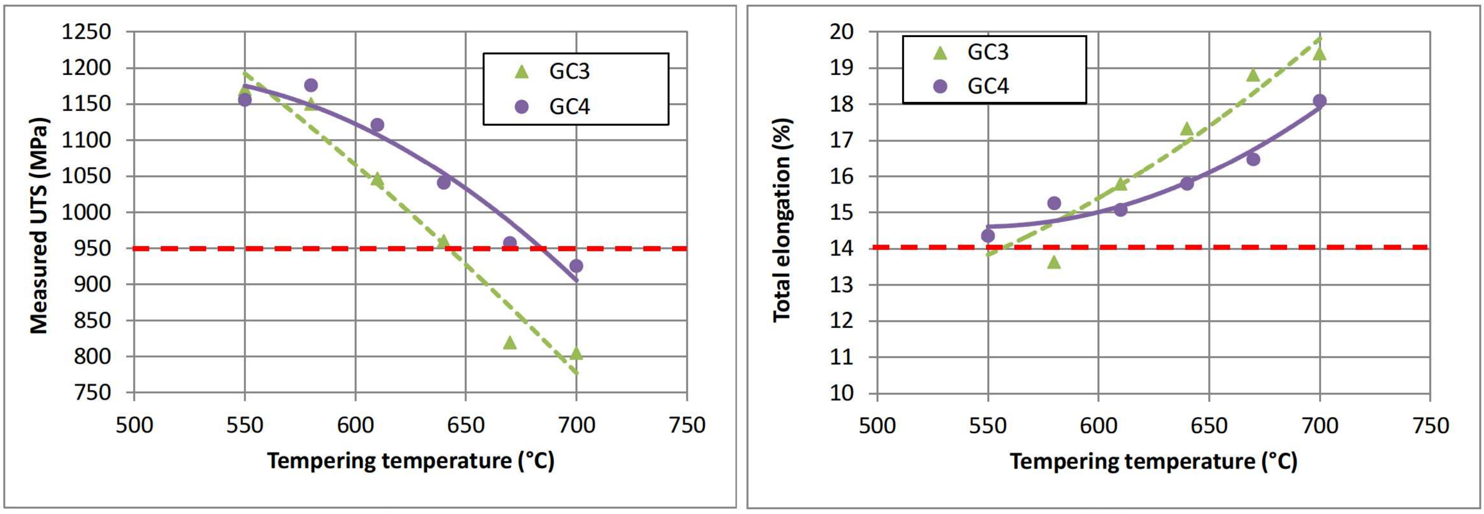
$M_{23}C_6$ forms at higher temperature and, in steels GC3 and GC4, it is the main phase formed during tempering treatments from 700 to about 600.

Tempering below 600°C produces a mixture of the two phases.($M_{23}C_6$ and M_7C_3)n

In absence of kinetic effects, it is expected that in the steel GC4 the M_7C_3 becomes the major precipitate phase below 600°C

Optimization of the materials performance

- With a tempering treatment at a temperature less or equal to 600°C, both the steels fulfil the requirements.
- From the viewpoint of the relationship between impact energy and UTS both materials comply with the standard
- GC3 has the best combination of strength and toughness for tempering temperatures of 580 and 550°C.



a) b)

Fig. 10. Measured UTS (a) and total elongation (b) of the steels GC3 and GC4 after quenching and 40 min tempering in the range 550 to 700°C. The horizontal dashed lines are the respective minimum acceptable values according to the reference standard for the component.

Conclusions

Optimum combination between **strength and toughness**, complying with the reference standard for the production of 300 bar gas cylinders, is represented by the steel **GC3** quenched and tempered at a temperature in the range from **580 to 550°C for 40 min**;

GC3 steel processed according to this route is has a **UTS** in the range between **1100 and 1200 MPa**, **elongation** of **14 to 16%** and an average **impact energy at -50°C between 50 and 60 J/cm^2**;

This result has been achieved by **enhancing the hardenability** and the **solid solution strengthening** of the alloy **without** exploiting any further hardening due to **vanadium additions**. This guarantees an excellent homogeneity of the fully martensitic microstructure, as obtained after oil quenching, by **avoiding** the formation of undesired **bainite**. In addition, the relative **low tempering temperatures** promote a **fine precipitation** of carbides which is fundamental for achieving the target toughness level.

Alessio Saccocci
Material Microstructure Throug
Engineering Manager

P. +39 06 5055310
M. +39 3487357006
e-mail alessio.saccocci@rina.org

Paolo Emilio Di Nunzio
Senior Scientist

P +39 06 5055917
e-mail paolo.dinunzio@rina.org

RINA Consulting - CSM S.p.A.
Via Di Castel Romano 100 - 00128 ROMA - ITALIA
rina.org