

Metallurgical Temperature Sensors

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Abstract: This short review article gives an overview of the use of several novel, metallurgical temperature sensors. These include the Feroplug, the Sigmaplug, the Templug and PETIT. Metallographic methods that utilise carbide segregation and the thickness of metal oxide scales that accumulate on steam boiler pipes are also introduced. Besides reviewing the various metallurgical sensors, emphasis has been placed on the Sigmaplug, which is a new, potentially patentable technique. A new application i.e. monitoring of temperature fluctuation and overheating/underheating, for an 'old' patented technique, the Feroplug, is also discussed in this article. New results on the Sigmaplug, some of which have not been published before, on this potentially patentable technique are presented in this article. Additionally, the latest results by the present group of authors on the use of metallurgy-related phenomena in stainless steels for temperature measurement are introduced. The Feroplug is an 'old' patented technique that was originally designed for the measurement of long-term average temperatures. Recently, attempts have been made to assess the possibility of using this technique for temperature fluctuation and overheating/underheating monitoring. Results on this topic are introduced.

Keywords: Feroplugs, Sigmaplugs, Templugs, PETIT, temperature sensors.

1. INTRODUCTION

The measurement of temperature in industry is of paramount importance. For instance, prevention of creep-related damage of components working at high temperatures hinges critically on whether an accurate (or reasonable at the very least) estimate of the working temperature of these components can be made. Figure (1) shows the creep rupture of a boiler header in a power plant. Had the temperature of the boiler header been properly monitored, its failure could have been averted. Overheating of piping in power plants and chemical plants must also be avoided, as their failure is also catastrophic. Nevertheless, if overheating is unavoidable and does occur, people must be notified in time in order to head off accidents and reliable monitoring of temperature fluctuation and overheating/underheating is thus valuable. Many more examples on the importance of temperature measurement can be enumerated.

There are a wide multitude of techniques for temperature measurement. Typical ones are thermocouples, metallic resistance thermometer detectors (RTDs), noise thermometers, etc. [1]. Some of these techniques are not prohibitively expensive, yet they provide very good accuracy and are usable in harsh environments. For example, the type S rare-earth thermocouple might be used up to 1760°C for short durations [2, 3] and the type T base-metal thermocouple may be accurate to about 1°C [3]. The Rh-Fe RTD can be used down to 0.5K [4, 5]. All of these techniques, under normal circumstances, can satisfy the requirements of most industrial applications.

1.1. The Merits of Metallurgical Temperature Sensors

While sophisticated techniques like the ones just mentioned are readily available, there are situations in which



Fig. (1). A boiler header whose failure was attributed to creep rupture after failure analysis.

their use may be cumbersome. Firstly, thermocouples and RTDs invariably involve connecting cables. Thus, using them to measure the temperatures of rotating parts of machinery will give a headache to operators as the connecting cables will get entangled. Secondly, when thermocouples and RTDs are used to probe the temperature of parts immersed in a corrosive medium, they must be used together with a protective sheath, which adds to cost.

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In view of the problems just mentioned, metallurgical temperature sensors like the Feroplug, the Sigmaplug, the Templug and PETIT stand out, as their use involves no connecting cables and electronic instruments. Further, the Feroplug and the Sigmaplug are simply pieces of stainless steel, so they are well-suited for use in corrosive environments without any protection, thereby incurring no additional costs.

In addition, in industry, a significant percentage of temperature measurements are done between 0 and 500°C [6], which falls roughly within the usable range of most of the metallurgical temperature sensors. Although metallurgical sensors are no match to thermocouples and RTDs in terms of accuracy and responsiveness, they are adequate for most industrial applications. This is because in a lot of industrial applications, an accuracy below 10°C may be acceptable [6], as maintenance workers may just need a rough estimate of temperature or whether overheating/underheating has occurred.

This article attempts to:

1. Give an overview of the most commonly used metallurgical temperature sensors;
2. Present the idea behind a potentially patentable technique, the Sigmaplug;
3. Introduce the latest results by the present group of authors on the use of metallurgy-related phenomena in stainless steels for temperature measurement; and
4. Give an account on the prospect of using the Feroplug for temperature fluctuation and overheating/underheating monitoring (the Feroplug was not originally designed for this purpose).

Even though most of the metallurgical temperature sensors are not recently-patented techniques, it is still worthwhile to have a short review of these novel, rugged temperature sensors, because review on this topic is very lacking in the literature.

2. METALLURGICAL TEMPERATURE SENSORS

2.1. The Feroplug

2.1.1. Use of the Feroplug for Temperature Sensing

The Feroplug technique is particularly useful for life assessment purposes in power and petrochemical plants, as they can reliably indicate the temperature of high-temperature components installed in these facilities [7-10]. This technique had undergone plant trials in a major European research project (BRITI-EURAM AMASS), in which the Feroplugs had been tested in a coal-fired boiler at ENDESA's Compostilla power plant in Spain and at EDP's Carregado power plant in Portugal. The Feroplug technique was patented in the USA, the UK and Europe, with financial and legal support provided by the British Technology Group, UK [7-9].

The Feroplugs are duplex stainless steels whose constituent phases are the ferromagnetic Fe-rich ferrite phase (α_{Fe}) and the paramagnetic austenite phase (γ). Figure (2) shows the typical microstructure of a Feroplug/Sigmaplug

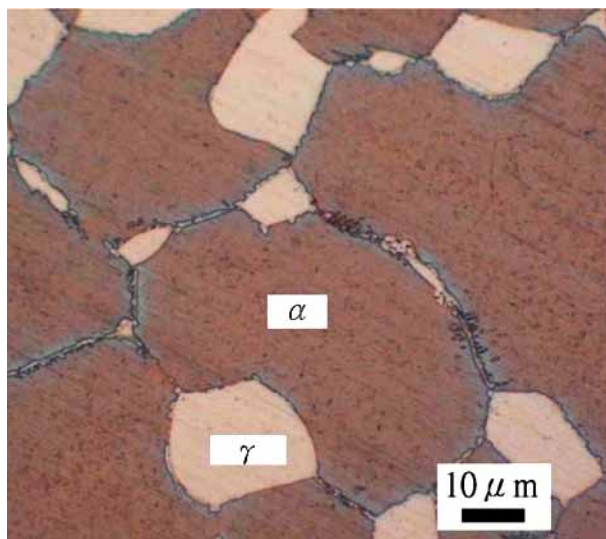
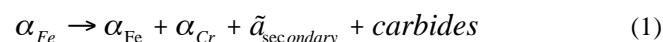


Fig. (2). Typical microstructure (after solution-treatment at 1100°C for 1h) of Feroplug/Sigmaplug alloy.

duplex stainless steel after solution-treatment. Feroplug alloys can be machined into any shape and size that suit a particular application. The Feroplugs are suitable for measuring the temperature of components working between 400°C and 600°C for extended periods (over thousands of hours) [11-14]. In this temperature range, the originally Fe-rich ferrite phase decomposes mostly into secondary austenite and Cr-rich ferrite:



Since the Cr-rich ferrite is not as ferromagnetic as its Fe-rich counterpart, the ferromagnetism of the Feroplugs diminishes (but will not vanish) as thermal ageing goes by. Nevertheless, the decomposition of the Fe-rich ferrite phase is incomplete between 400°C and 600°C, and so remnant Fe-rich ferrite is always present even after very prolonged exposure in this temperature range. The amount of remnant Fe-rich ferrite may be obtained by employing a ferriscope or a magnetic susceptometer, for example. Experimentally, it has been determined that the amount of remnant ferrite is dependent upon the ageing temperature. Figure (3) [15] illustrates the dependence of the amounts of remnant ferrite on different ageing temperature for a certain Feroplug alloy (composition in wt%: C-0.048, Si-0.52, Mn-1.56, P-0.004, S-0.005, Cr-25.6, Mo-0.02, Ni-8.06, Cu-0.02).

Figure (3) is in fact a representative Feroplug calibration graph. Suppose that a piece of Feroplug alloy pertaining to Fig. (3) is attached to a certain high-temperature component. When the Feroplug is retrieved afterwards and with the aid of Fig. (3), one shall be able to work out the working temperature of the component. For instance, if the Feroplug alloy is retrieved after being in contact with the component for 4000 hours, then the ferrite reading of the Feroplug material should be around 10. With this value, one may read from Fig. (3) that the Feroplug was thermally aged at about 550°C. Insofar as the Feroplug alloy was previously in contact with the component, the working temperature of the

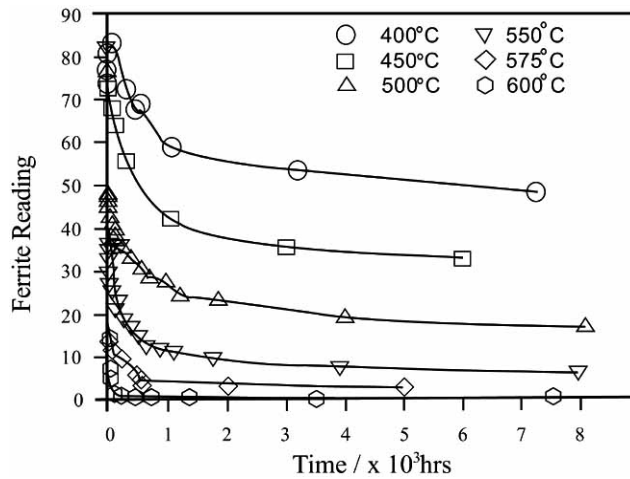


Fig. (3). The amounts of remnant ferrite in a certain type of Ferroplug material upon prolonged ageing at different temperatures [15].

component should be about 550°C, too. Tests conducted at Unit 1 of the Lamma Island Power Station of the Hong Kong Electric Co. Ltd. in Hong Kong showed that the accuracy of the Ferroplug technique at 520°C was about 3% [12].

2.1.2. Use of the Ferroplugs for Temperature Fluctuation Monitoring

Lately, it has also been suggested that the Ferroplugs could possibly be used for indicating temperature fluctuations and overheating [16]. Suppose that the temperature of a certain component, to which a piece of Ferroplug alloy has been affixed, changes from T_1 to T_2 at time t^* . Before t^* , the dissolution behaviour of ferrite obeys the calibration curve corresponding to T_1 , whereas after t^* , the dissolution behaviour of ferrite shall be governed by the calibration curve corresponding to T_2 . By measuring the ferrite content of the Ferroplug on a regular basis, the temperature fluctuation may be traced as delineated below.

Figure (4) shows two calibration curves corresponding to 500°C and 600°C. This figure shows that the temperature fluctuation at time $t^* \sim 100$ h can be clearly indicated. In this case, if the Ferroplug had been fixed to a component, then the jump between two calibration curves in Fig. (4) would have implied that the component had undergone an underheating of 100°C at 100h.

However, the use of the Ferroplug technique for temperature fluctuation is not without limitations. Since the dissolution of ferrite to secondary austenite and the sigma phase is a phase transformation process, it does take time. Therefore, if the temperature fluctuates from T_1 to T_2 and then returns to T_1 after a very short time (note that in Fig. (4), the temperature fluctuates from $T_1 = 500^\circ\text{C}$ to $T_2 = 600^\circ\text{C}$ and stays at T_2 thereafter), then the phase transformation process might not be responsive enough to record this short-lived temperature change.

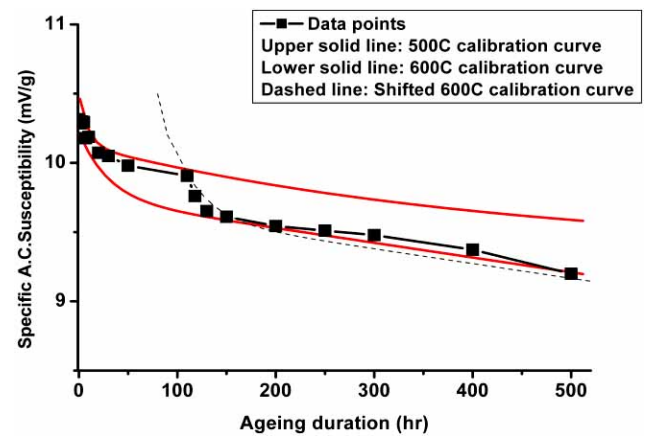
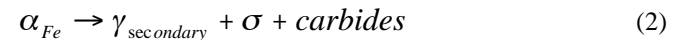


Fig. (4). The ability of the Ferroplugs to reflect temperature fluctuation [16].

2.1.3. Upper Working Temperature of the Ferroplugs

While the Ferroplug technique is very suitable for use between 400°C and 600°C, it is useless above 600°C. This is because in the range of 600°C and 900°C, instead of following reaction (1), the ferrite phase shall decompose completely according to reaction (2), i.e., the ferrite will almost transform entirely to secondary austenite and the intermetallic sigma phase (σ).



All of the transformation products in reaction (2) are paramagnetic (non-magnetic) at ambient temperature. Because of the complete dissolution of the ferromagnetic ferrite phase on extended thermal ageing, the Ferroplugs will eventually become paramagnetic, irrespective of the ageing temperature between 600°C and 900°C. Figure (5) shows that the calibration curves, obtained by measuring the a.c. magnetic susceptibility of the aged Ferroplugs samples, corresponding to 700°C and 800°C for a certain Ferroplug alloy, all converge to near zero after extended ageing. Therefore, there is no way to distinguish between the two curves and so room-temperature magnetic measurement will not be able to tell whether the Ferroplug had been thermally aged at 700°C or at 800°C. In short, the Ferroplug technique fails!

2.2. The Sigmaplugs

Since the temperature range of 600°C and 900°C, where the Ferroplugs are useless, is also of importance in industry, efforts aiming at extending the use of duplex-stainless-steel temperature sensors to this range have been on-going. Some preliminary results have been obtained by our group and the technique is named the Sigmaplugs. The Sigmaplug technique utilises the intermetallic sigma. In addition to the sigma phase, another commonly found intermetallic phase of stainless steels, the chi phase, has been found to possess the

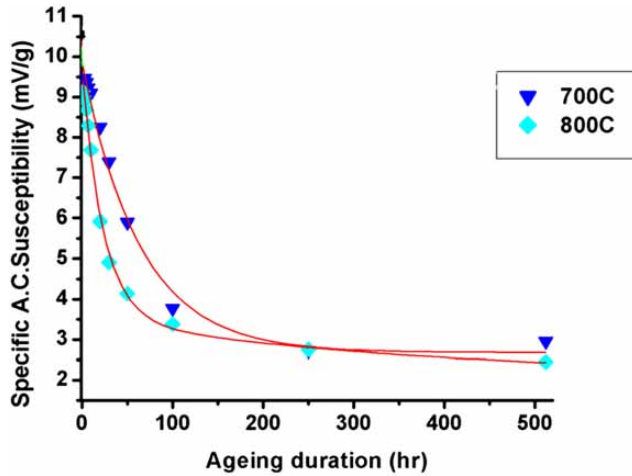


Fig. (5). Tendency of the calibration curves of the Feroplugs to converge to near zero after prolonged ageing between 600°C and 900°C.

potential of being used for temperature sensing, too. Research efforts have been ongoing in earnest to assess the feasibility of using these intermetallics for temperature sensing and it is believed that these techniques are potentially patentable. Like Feroplug alloys, Sigmaplug alloys can be fabricated into any shape and size that suit a particular application, thus offering flexibility.

Recent studies have found that both the cryogenic magnetic transition and the high-temperature dissolution of the sigma are potentially employable for temperature measurement.

2.2.1. Temperature Measurement Using the Cryogenic Magnetic Transition of the Sigma Phase

As depicted in reaction (2), one of the main transformation products in duplex stainless steels between 600°C and 900°C is the intermetallic sigma phase. The sigma phase is paramagnetic at room temperature, but has been found to undergo a paramagnetic-to-ferromagnetic transition at cryogenic temperatures (at about the liquid nitrogen temperature 77K) Fig. (6) [17, 18].

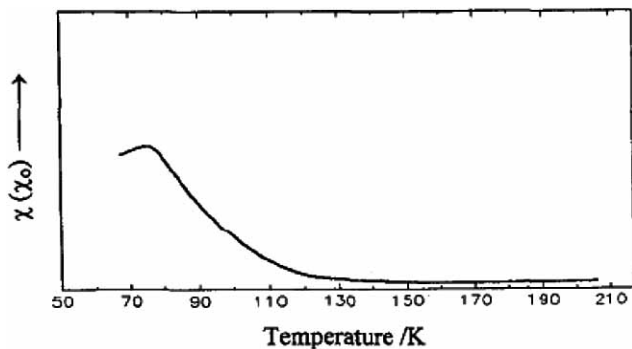


Fig. (6). The cryogenic paramagnetic-to-ferromagnetic transition of the sigma phase for a Sigmaplug duplex stainless steel [18].

It was believed that the characteristic temperatures (the onset temperature of transition, the Curie temperature and the paramagnetic Curie temperature) of this transition would depend on the composition of the sigma phase, which in turn depends on the thermal ageing temperature [19]. So, it was conjectured that these characteristic temperatures might be utilisable for deduction of the prior ageing temperature of the aged duplex steels. Preliminary results obtained by the present group of authors have confirmed this conjecture.

Figure (7) illustrates the temperature dependence of the Curie temperature of the sigma phase of the duplex stainless steel 7MoPLUS[®] produced by Carpenter Ltd. This figure may serve as a calibration graph for temperature monitoring. It has been found that the paramagnetic Curie temperature and the onset temperature of transition also show relatively well-defined temperature dependence as that shown in Fig. (7) (results on this topic shall be published elsewhere very shortly).

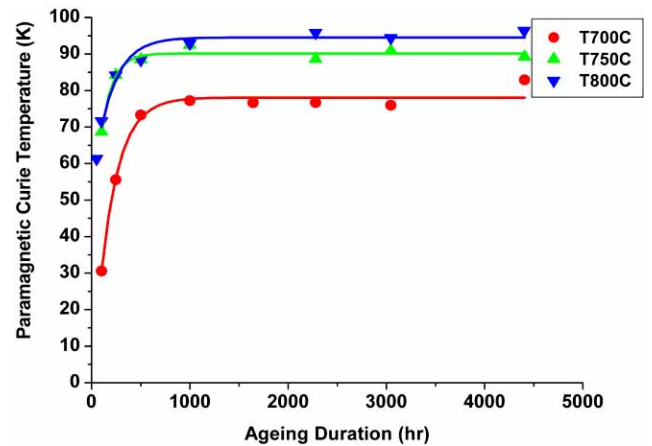


Fig. (7). Variation of the Curie temperature of the sigma phase of duplex stainless steel 7MoPLUS[®] [19].

Besides being used as temperature sensors, preliminary plant trials have demonstrated that the Sigmaplug technique (using another duplex stainless steel other than 7MoPLUS[®]) is usable for hotspot indication [17]. Figure (8) shows how a piece of Sigmaplug duplex stainless steel is fixed to a boiler pipe during the plant trials.

Besides the sigma phase, it has been found that the chi phase of the austenitic stainless steel 316L also undergoes a cryogenic magnetic change and its Neel temperature also exhibits dependence on its prior ageing temperature Fig. (9) [20].

2.2.2. Temperature Measurement Using the High-Temperature Dissolution of the Sigma Phase

As just introduced, while the cryogenic magnetic measurement of the sigma phase of duplex stainless steel might possible be used for temperature sensing, the cryogenic measurement is inconvenient to conduct (on grounds that liquid nitrogen has to be used). Very recently, the present group of authors have discovered that the high temperature dissolution of the sigma phase might also have the potential of being used for temperature measurement.

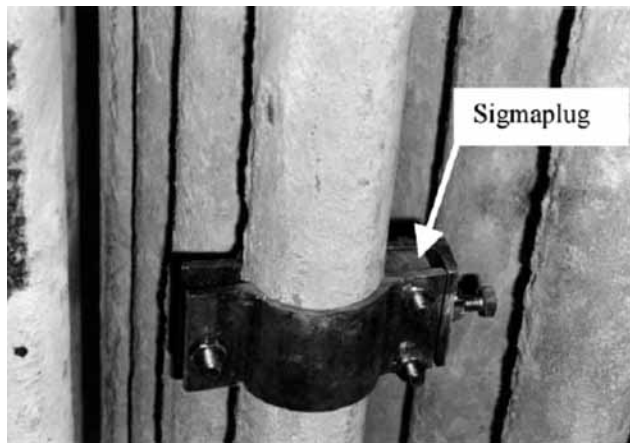


Fig. (8). Photograph showing how a Sigmaplug alloy is fixed to a boiler pipe such that the two will be in thermal contact [17].

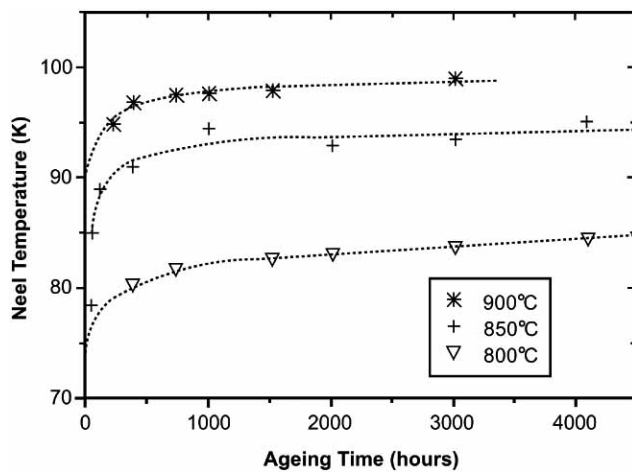


Fig. (9). Variation of the Neel temperature of the chi phase of an AISI316 austenitic stainless steel with ageing duration and temperature [20].

Upon heating, the sigma phase shall dissolve and this dissolution requires absorption of thermal energy. So the dissolution may be sensitively and accurately studied by thermal analysis (using DTA or DSC). Figure (10) shows typical DTA thermographs of samples that had been aged at 973K for various durations (the samples contained mostly secondary austenite and the sigma phase). From Fig. (10), one can see that the DTA curves shall gradually shift to higher temperature as ageing goes by. So, the characteristic temperatures, i.e., the peak temperature T_p and the onset temperature of transition T_s as defined from the DTA curves, can reflect the prior ageing temperatures of the samples and so might be employed for temperature measurement Fig. (11). The shift in position of the DTA curves has to do with the changing composition and morphology of the sigma phase Fig. (12) [21].

The use of Fig. (11) is as follows: when one wants to measure the temperature of a high-temperature component, he/she can attach a piece of Sigmaplug duplex stainless steel to the component. The Sigmaplug is retrieved afterwards and

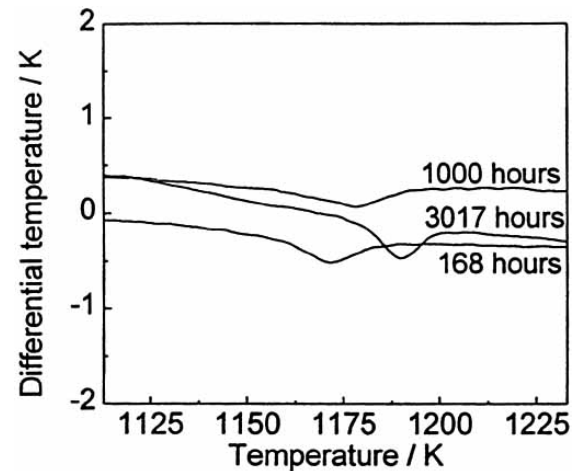


Fig. (10). DTA curves showing the dissolution behaviour of the sigma phase obtained after thermal ageing at 973K for different durations [21].

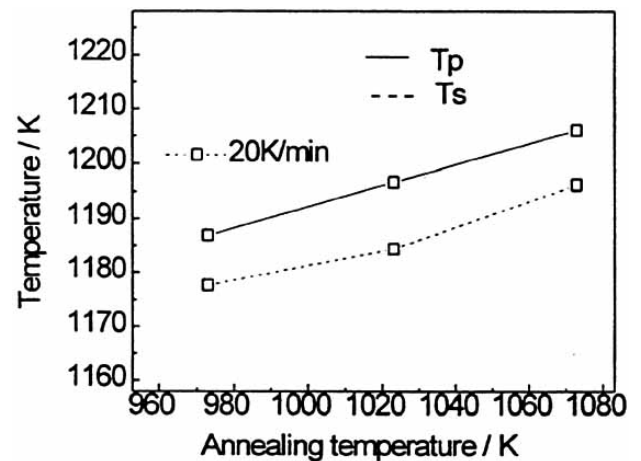


Fig. (11). The peak temperature T_p and the onset temperature of transition T_s obtained from the DTA curve for a Sigmaplug alloy that had been aged at 973K for 168h (the sample was heated at a rate of 20K/min) [21].

then put to DTA test. Now, suppose that the peak temperature T_p obtained from DTA test is about 1206K, then from Fig. (11), one can deduce that the Sigmaplug, which was in thermal contact with the component, was subjected to an ageing temperature of about 1072K. The T_s curve in Fig. (11) may be used in a similar fashion.

2.3. The Templug

The Templug technique was developed jointly by Testing Engineers Inc. and Shell Research Ltd. in the early 1970s [22]. The Templugs are made of alloy steels. When the Templugs are thermally aged at high temperatures, their microstructural changes result in hardness change. The hardness of the Templugs has a very well-defined dependence on ageing temperature and duration and a mock calibration graph is shown in Fig. (13). Suppose that a Templug has been in thermal contact with a component for time t_1 and that its hardness has been found to be H_1 after removal from the component. Then from the calibration

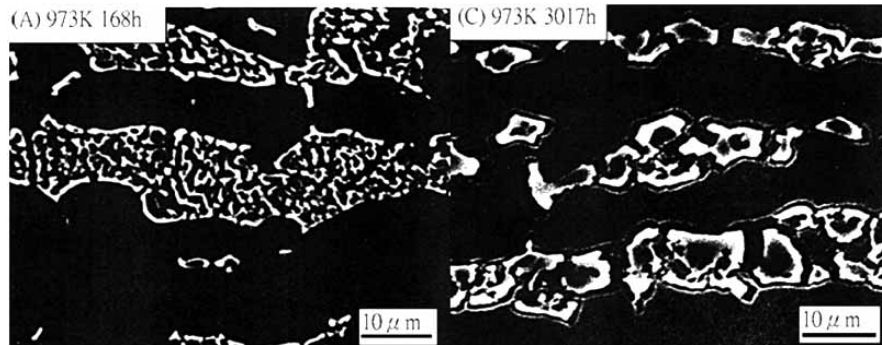


Fig. (12). Micrographs showing the coarsening of the sigma phase in a Sigmaplug alloy that had been aged at 973K for 168h and 3017h, respectively [21].

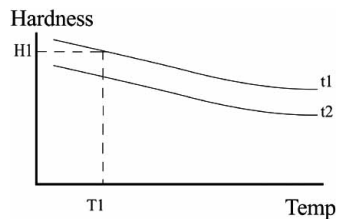


Fig. (13). A mock calibration graph for the Templugs.

graph, one may deduce that the prior ageing temperature of the Templug, which was also the temperature of the component at the time when it was in contact with the Templug, is T_1 .

As regards to accuracy, Bramman *et al.* [23] reported that the accuracy of was about 15°C at in the range of $450\text{--}600^\circ\text{C}$ at up to 5000 h, and about 25°C between $600\text{--}650^\circ\text{C}$ at up to 2000 h. Supplier of the Templugs stated that accuracy could reach 3% within the valid measuring range under the most favourable condition [24].

2.4. PETIT

PETIT is the acronym for Plant Effective Temperature Implantation Technique, which may indicate the creep effective temperature of components. This technique was the brainchild of the Engineering Investigations Department of ESKOM in South Africa and is now maintained by ERA Technology, Ltd, UK [25].

PETIT is a solid state bimetallic diffusion couple that is composed of copper and gold. The PETIT couple is cylindrical (2 mm long and 0.5 mm - 1 mm in diameter), with gold as the core and copper the outer tube. There is a stainless steel protective sheath and the whole sheathed couple is inserted into a 17% Cr ferritic hexagonal stud. The stud is welded to the component of interest by using a capacitive discharge process [25]. On completion of measurement, each PETIT couple is sectioned and its radial diffusion profile analysed by using energy dispersive X-ray (EDX). The temperature at which the PETIT stud was aged can then be deduced from the diffusion profile.

Like the 'plugs' mentioned above, the use of PETIT involves no clumsy cabling whatsoever. The time of

exposure of PETIT measuring couples can be up to 50000 hours and the measuring range is from 450°C to 700°C [25].

2.5. Metallographic Method

2.5.1. Carbide Segregation

Exposure of alloy steels, such as 1Cr-0.5Mo steel, for long periods at elevated temperatures may induce a number of microstructural changes, including the precipitation and growth of carbides. The change in the spacing of carbide particles gives an indication of the average temperature of the metal. Experimentally, it has been found that the average distance between carbide particles is given by [26]:

$$\lambda_r^3 = \lambda_0^3 + C_0 \exp(\beta T t) \quad (3)$$

where

λ_t is the average intercarbide spacing at time t

λ_0 is the initial intercarbide spacing

T stands for temperature

C_0 and β are constants

Since the alloy contents of the carbides of this type of steel will usually get higher and higher as thermal ageing proceeds [27], the ageing temperature may also be deduced by measuring the lattice parameters of the carbides.

2.5.2. Steam-Side Oxide Film Thickness

For metal boiler tubes carrying relatively pure steam, the steam temperature may be approximately deduced from the thickness of the oxide scale on the steam side of the tubes. The thickness of the oxide scale can be measured non-destructively by using ultrasonic technology. A number of laws governing the growth of oxide scale on the steam side are available in the literature, one of which is as follows [28]:

$$\begin{aligned} \log(x) &= A + B(LMP) \\ x^2 &= kt \\ x &= \frac{At}{B + Ct} + Dt \end{aligned} \quad (4)$$

Where x is the thickness of the oxide scale on the steam side

t is the time of exposure

T is the steam temperature in the Ramline scale

A, B, C and D are constants

LMP is the Larson-Miller parameter
 $LMP = T[20 + \log(t)] \times 10^{-3}$ [29]

Some of difficulties inherent to this method are: 1. because the oxide scale may be disrupted by chemical attack, its thickness can be difficult to measure accurately at times and 2. Since a number of formulae governing oxide-growth have been proposed, the operator must judiciously decide which one to use, which can be subjective. The error of this approach may range from 20°C to 30°C.

3. CONCLUDING REMARKS

Patents for novel temperature sensors have also been filed recently. Systems, methods, and heaters for treating a subsurface formation and systems/methods for making heaters are described. At least one heater includes a ferromagnetic conductor and an electrical conductor. The electrical conductor is electrically coupled to the ferromagnetic conductor and the heater provides the first amount of heat at a lower temperature. The heater may provide a second reduced amount of heat when the heater reaches a selected temperature, or enters a selected temperature range, at which the ferromagnetic conductor undergoes a phase transformation [30]. Heaters for treating a subsurface formation can be obtained by using the systems and methods recently invented. The heater includes a heater section including iron, cobalt, and carbon. The heater section has a Curie temperature less than a phase transformation temperature. The Curie temperature is at least 740°C. The heater section provides, when time varying current is applied to the heater section, an electrical resistance [31]. System, methods, and heaters that include the high strength metal alloys including chromium, nickel, copper, manganese, silicon, niobium, tungsten and iron have been described. At least one heater system may include a canister at least partially made from material containing at least one of the metal alloys. At least one system for heating a subterranean formation may include a tubular that is at least partially made from a material containing at least one of the metal alloys [32].

The choice of a suitable temperature sensing technique for a particular application will be affected by a jumble of factors. Some of these are:

- Feasibility and ease of installation
- Cost of implementation
- Speed
- Operational skill required

Although a lot of techniques offering higher accuracy than metallurgical temperature sensors do exist, the latter still stand out under some circumstances. For instance, the use of the 'plugs' and PETIT just involves attachment of them to the component of interest, and there are no cabling and electronics involved. As a consequence, these metallurgical temperature sensors are rugged and very well adapted for use when the components to be measured are constantly moving and are of complex geometry (the use of thermocouples might be out of the question in this case).

Additionally, metallurgical sensors are not bulky and so they do offer flexibility and ease of installation. Another advantage of these metallurgical techniques is their comparatively low costs.

The use of the Templugs involves hardness measurements, while PETIT has to be used alongside EDX analysis and the Sigmaplugs require either cryogenic magnetic measurement or DTA tests. Therefore, all of them are relatively time-consuming to use and may require operational skills of the user. For the Feroplugs, portable and easy-to-use ferrite content measuring devices like the Ferritscope are readily available and so this technique is not cumbersome to use.

Responsiveness seems to be a drawback that plagues all of the metallurgical temperature sensing methods introduced in this article. The 'plugs' and the carbide-segregation method all utilise metallurgical phase transformations which do take time. And so they are not suited for measuring instantaneous temperature. The use of PETIT relies on solid state diffusion and thus is also a time-consuming technique. Needless to say, the method that relies on the measurement of the thickness of metal oxide scale on the steam side of piping also cannot be used to indicate the instantaneous temperature of the piping.

Nonetheless, the methods discussed in this article are very suitable for indicating the long-term average temperature of components. Furthermore, all of them are deployable in very hostile environments.

CURRENT & FUTURE DEVELOPMENTS

To the present authors' knowledge, it seems that not many groups are working on metallurgical sensors currently, as judged from the number of articles published in relatively popularly-circulated scholarly journals. Current efforts mainly focus on finding suitable Fe-Cr-Mo alloys (duplex stainless steels and austenitic stainless steels) whose sigma phase possesses the desired cryogenic magnetic transition. The desired cryogenic magnetic transition should exhibit characteristic temperatures that are widely spaced.

As regards future research direction, it has very recently been found that the high-temperature dissolution of the sigma phase might possibly be used for temperature measurement, too. Preliminary results suggest that if the sigma phase exhibits the desired dissolution behaviour, the onset temperature of dissolution and peak temperature of dissolution, as measured by using DTA or DSC, might conveniently be used for temperature measurement. Future efforts will focus on verifying further these preliminary results. Similarly DTA or DSC measurements shall also be repeated on the sigma phase of austenitic stainless steels.

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