

# EFFECT OF NANOMATERIAL ADDITION USING GMAW AND GTAW PROCESSES

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**Abstract.** The need for industries to remain competitive in the welding business has created a necessity to develop innovative processes that can exceed customers' demand. Significant improvements in weld efficiency during the past decades still have their drawbacks, specifically in weld strength properties. Recent innovative technologies have created the smallest possible solid material, known as nanomaterial, and its introduction in welding production has improved the weld strength properties and overcome unstable microstructures in the weld. This study critically reviews the methods of introducing nanomaterial to the weldments and the characteristics of the welds produced by GMA (gas metal arc) and GTA (gas tungsten arc) welding processes. The study mainly focuses on changes in the microstructural formation and strength properties on the welded joint and also discusses the factors influencing such improvements due to the addition of nanomaterials. The literature review shows that the effect of nanomaterial addition in the welding process modifies the physics of the joint region, thereby resulting in significant improvement in the strength properties, with a stable microstructure in the weld. In general, the factors that have a major influence on joint strength are the dispersion, characteristics, quantity and selection of nanomaterials. The nanomaterials addition does not affect the fundamental properties and characteristics of the base metals and the filler metal. However, in some cases, the addition of nanomaterials leads to the deterioration of the joint properties by unstable microstructural formations. Research is still being conducted to achieve high weld properties in various materials through different welding processes and on other factors that influence joint strength.

## 1. INTRODUCTION

In the manufacturing field, various processes (such as machining, drilling, riveting, forming, moulding and welding) have been intensively developed to generate quality products economically. Welding is one of the most important processes in manufacturing, and welding processes have been significantly improved. For example, the construction of complex structures requires joining performed by welding. The strength of the whole complex structure is determined by the strength of the joined region. The welding process, however, reduces the

material properties while joining. As the joining of two materials involves some complex issues and problems, various studies have been carried out to improve the weld joint and reduce problems in joining materials. Recently, nanomaterials have been introduced in the welding process to improve the joint properties. The addition of nanomaterials has not only fulfilled the demands set on welding by the industries, but also revolutionised the materials.

Due to the nanomaterial size factor, however, there are issues to consider when introducing nanomaterial into welding [1]. Problems have been solved by manufacturing welding electrodes and filler

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metal, as well as coating on base metals with added nanomaterials (i.e. nanopowders and nanowires). The usage of nanomaterial-added materials improves the weld properties and reduces defect formations [1]. For instance, the welding of aluminium and its alloys by the TIG process with multi-walled carbon nanotubes (MWCNTs) added in the filler material produced a joint with better mechanical properties and reduced defect formations compared to a weld formed with no added MWCNTs in the filler material [2]. Moreover, several studies show that adding nanomaterials in the filler metal improves the joint strength of welding electrodes [3,4]. Therefore, better weld properties have been established by the addition of nanoparticles to joints [5].

There are various nanomaterial classifications, but the mostly required nanomaterials in welding production are nanoparticles and nano-carbonaceous elements [6]. Metal oxide, ceramic carbides, rare element oxide and silver are some of the nanoparticles used in welding production.

Addition of nanomaterials to the joining materials has created a need to understand the effect of nanomaterials on the weldments. This study reviews the literature about the ways of introducing nanomaterials to the joint in GMAW and GTAW processes, as well as the nanomaterial effect on the weld microstructural change, weld properties and weld appearance. Moreover, this study focuses on the factors that lead to changes in the weld microstructure, such as grain refinement, phase change in the microstructure, precipitation at the grain boundaries, as well as weld strength properties, such as improvement in hardness, tensile strength, impact strength, corrosion resistance strength and wear resistance. However, other effects and factors in the weld metal formed with nanomaterial added are yet to be examined.

## **2. NANOMATERIALS USED AS COATING IN WELDING ELECTRODE IN GMAW PROCESS**

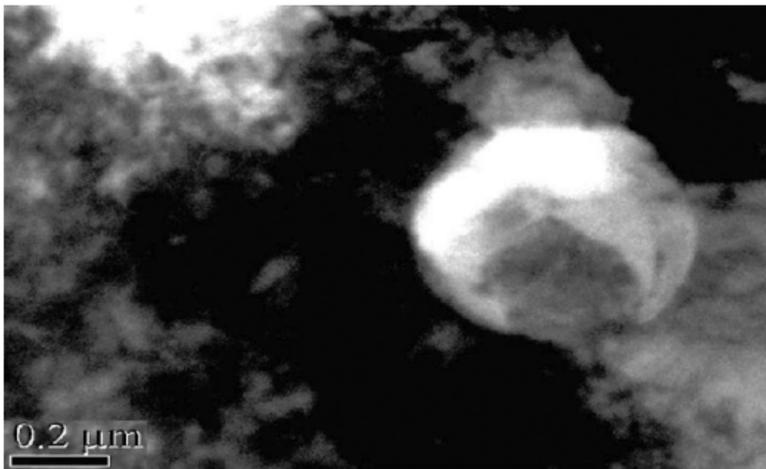
Because of the increasing demand of high-strength metals in various applications, their joining requires extraordinary material insertion to improve their characteristics. For welding sophisticated metals, nanomaterials improve the properties of the weld metal [7]. As the GMAW process is the most commonly used welding method in the industries and manufacturing sites, the introduction of nanomaterials into the welding process has been realised with welding electrodes. The nanomaterials have been mixed in the flux of the welding elec-

trode, in which the core wire of the electrode has a coating with a nanomaterial-mixed flux. The nanoparticle-coated electrodes are employed in welding high-strength structural steels and other special metals to achieve weld deposits with greater strength and better properties. For instance, toughness properties are a major issue with high-strength structural steels; improving this property in the structural steel requires the microstructural control and nucleation of grain boundaries [8,9], which is possible through the addition of nanoparticles into the joint.

A previous study stated that the GMAW process with titanium microparticles added in the welding electrodes exhibited weld metal formation with better properties. Grain refinement was attained by reduced particle size due to the increased pinning effect by the microparticles added [10]. The reason for selecting Ti particles instead of other elements is because of their nucleation characteristics, grain refinement, high melting point and stability, as well as increases in the recovery element during solidification [11-13]. However, titanium oxide formation or addition has a negative aspect, since non-metallic addition in the weld metal reduces the corrosion resistance by pitting action [14]. The nanoparticle coating in the welding electrode has various advantages over conventional electrodes, for example, stable transfer in the molten droplet consisting of nucleation elements (i.e. Ti) [15,16]. This nucleation element assists in the grain refinement and nucleation of the microstructure leading to property improvement. As the nanoparticle coating on the electrode has been used for the stabilisation of molten droplets, the addition of nanoparticles would provide improvement in the properties of the weld metal.

## **3. EFFECT OF NANOPARTICLE-COATED ELECTRODE ON WELD METAL CHEMICAL COMPOSITION**

Weld metal composition is one of the factors that determine the weld microstructure and properties by the alloying elements present in the weld. Moreover, the weld composition is homogeneous by the dilution of the base metal; however, filler metal addition modifies the chemical composition. For instance, carbon steels welded by the E11018M electrode coated with TiO<sub>2</sub> nanoparticles had a different chemical composition compared to the weld metal formed without nanoparticles added in the electrode. Elements such as Mn, Ni and Mo have been recovered in the weld metal produced by the electrode coated with TiO<sub>2</sub> nanoparticles. The presence of the



**Fig. 1.** Mn complex inclusion in the weld metal of low alloy steel using  $\text{TiO}_2$  nanoparticles. Reprinted with permission from C. Chen, H. Xue, H. Peng, L. Yan, L. Zhi and S. Wang // *Journal of Nanomaterials* **2014** (2014) 1. (c) 2014 DeepDyve, Inc.

elements was due to the  $\text{TiO}_2$  nanoparticles that aided in the reaction of the slag metal due to the size of the particles. However, the Cr element in the weld composition formed by the electrodes was reduced, which was due to the Ti reducing corrosion resistance [15].

The slag metal reaction due to the generation of more oxygen molecules ( $\text{O}_2$ ) by the detachment of the Ti elements from the  $\text{TiO}_2$  nanoparticles also resulted in the disappearance of elements [17]. This occurred on the weldments of low-alloyed steels by the increased  $\text{O}_2$  content resulting in a faster degradation of the Mn, C, P, S and Si contents, due to oxide formations [18]. The degradation of elements in the weld metal was also noted in the experiment by Fattahi et al. [19] on welding low-carbon steels by multi-passing with the  $\text{TiO}_2$  nanoparticle-coated electrode. The weld metal formed showed a decrease in the composition of elements, such as Si, Mn, and C, compared to the weld metal without nanoparticles. However, instead of forming Mn metal oxide, the Mn was combined with Ti forming complex inclusions, which had a significant effect on the microstructure. The complex inclusion in the weld metal exhibited a composition of titanium oxide as the black core and manganese oxide as the outer layer around the core, shown in Fig. 1. This complex inclusion had a positive effect on the nucleation site for redistribution of elements [16].

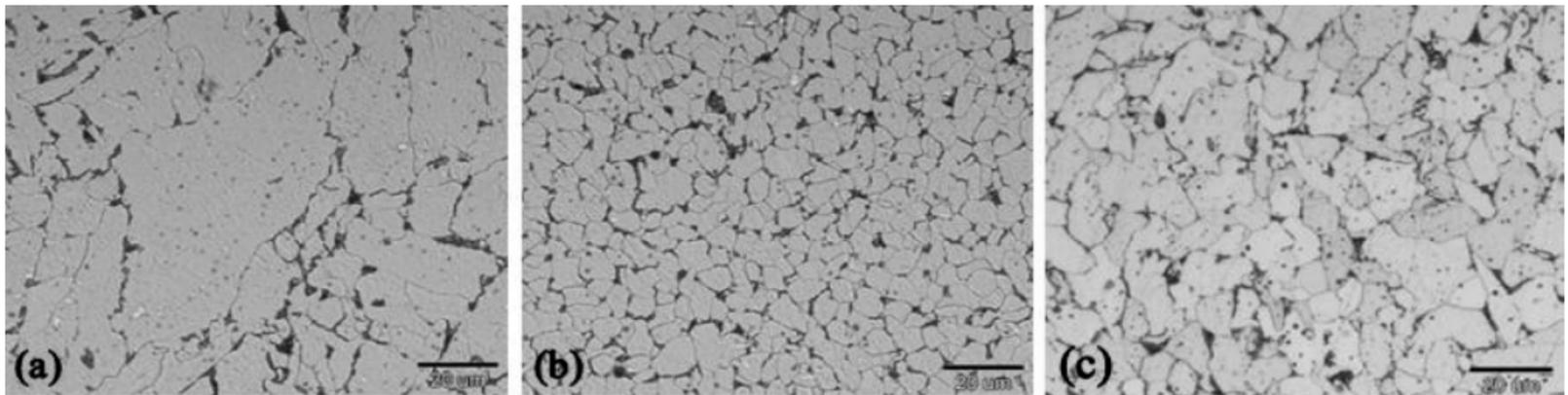
This complex inclusion forms with high oxygen content; however, in the case of low oxygen content, Chen et al. [16] showed that welding low-alloyed steel while melting formed a stable  $\text{Ti}_3\text{O}_5$  phase, rather than a  $\text{TiO}_2$  phase. The  $\text{TiO}_2$  phase only forms with very high oxygen content, which is above 0.0077% [20].

Hence, observations show that elements have been recovered in the steel weld metal by nanoparticle addition through slag metal reaction, depending on the oxygen content. However, slag metal reaction also resulted in the degradation of element composition in the weld and complex inclusions in welds. As the  $\text{TiO}_2$  nanoparticles generate oxygen content in the weld pool through the detachment of Ti, the amount of nanoparticles added plays a vital role in the chemical composition of the weld metal.

#### 4. EFFECT OF NANOPARTICLE-COATED ELECTRODE ON WELD MICROSTRUCTURE

In the steel microstructure, the ferrite microstructural phase has a beneficial effect, since it improves the properties and stability of the steel weld joint. Achieving acicular ferrite microstructural phases requires the dispersion of nucleation sites that consecutively depends on the thermodynamic properties of liquid metal [21]. Moreover, there are other factors inducing the formation of acicular ferrite, such as the grain size of austenite structure, alloying elements and the cooling rate of the weld metal [22-24]. Early research showed that without active inclusion in the weld, the occurrence of acicular ferrite formation is hardly possible [25]. Ti is one of the activating elements in weld metal for the formation of the acicular ferrite phase compared to other metallic inclusions. Moreover, Ti aids in grain refinement for better weld metal formations [26,27].

As studies showed, the alloying element and grain size influence acicular ferrite formation, and the quantity of nanoparticles added in the welding electrode varies the alloying element and has a great impact in the microstructure of acicular phase formation. Fattahi et al. [18] showed that welding low-carbon steel with increasing the  $\text{TiO}_2$  nanoparticle content in the electrode decreased the ferrite grain boundary and improved the acicular and Widmanstatten ferrite contents. A low amount of  $\text{TiO}_2$  nanoparticles (i.e. 0.006 wt.%) in the weld exhibited ferrite grain boundaries, a high amount of Widmanstatten ferrite and acicular ferrite compared to the weld metal without nanoparticles. The high Widmanstatten ferrite content was due to the cooling rate variation and low amount of complex inclusions [28,29]. A medium content of  $\text{TiO}_2$  nanoparticles (i.e. 0.023 wt.%) in the weld resulted in higher acicular ferrite content and a small amount of ferrite grain boundaries. However, a high content of  $\text{TiO}_2$  nanoparticles (i.e. 0.027 wt.%) in the weld



**Fig. 2.** Weld beads microstructural formation of low carbon steels with (a) low, (b) medium, and (c) high  $\text{TiO}_2$  content nanoparticles. Reprinted with permission from M. Fattahi, N. Nabhani, M. R. Vaezi and E. Rahimi // *Materials Science and Engineering: A* **528** (2011) 27. (c) 2011 Elsevier B.V.

exhibited more Widmanstätten ferrite and ferrite grain boundaries with an increase in grain growth compared to the weld without nanoparticles. This grain growth resulted in coarse grains, which was due to the increase in the reheated zone by arc constriction [18].

The phenomenon of increased acicular ferrite content after a nominal amount of nanoparticles added has also been noted in the welding of carbon steel with multi-pass on the weld metal by an electrode coated with  $\text{TiO}_2$  nanoparticles [10,19]. Due to the multiple passes, the weld metal showed a columnar grain zone and reheated grain zone. The reheated grain zone exhibited both coarse grains and fine grains that had no effect until with variation in the  $\text{TiO}_2$  nanoparticles in the welding electrode [10,19], illustrated in Fig. 2. Fig. 2 shows that the microstructure formation by the medium content of  $\text{TiO}_2$  nanoparticles in the weld metal produced more fine grain structures compared to the low and high  $\text{TiO}_2$  content nanoparticle weld metals. The main reason for the fine grains is the oxide particle refinement, which leads to a very fine intergranular ferrite grains by nanoparticle addition [18].

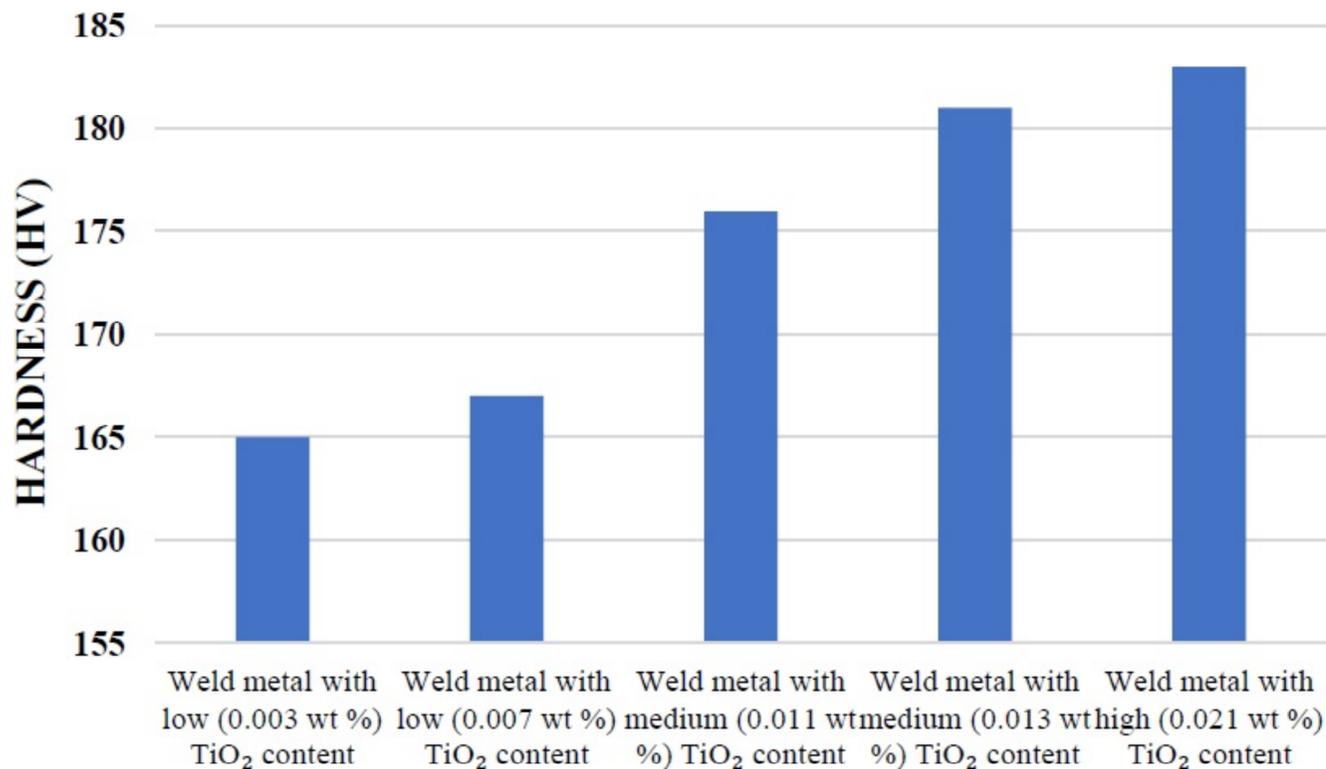
The studies show variation in the grain size between the steel weld metals formed with varying contents of  $\text{TiO}_2$  nanoparticles in the electrodes, which is shown in Fig. 2. The variation in grain size was due to the low quantity of complex inclusions, weld metal cooling rate, increase in nucleation sites and improvement in arc stability by the  $\text{TiO}_2$  nanoparticles added. Moreover, multiple passes in the weld produced significant variation in the grain size.

To identify the effects and factors of complex inclusion in the weld microstructure, Pal and Maity [15] welded carbon steel by  $\text{TiO}_2$  nanoparticles added in the welding electrode resulting in complex inclusion formation while solidification. This complex inclusion in the weld led to fine grains and more

acicular ferrite structures compared to the weld metal formed without  $\text{TiO}_2$  nanoparticles. Fine grains with a significant content of acicular ferrite structures have been supported by a turbulent flow in the weld pool. Chen et al. [16] also found similar acicular ferrite formation when welding low-alloy steel with an electrode coated with  $\text{TiO}_2$  nanoparticles. Moreover, Chen et al. [16] investigated the complex inclusion formations and showed that the particles of the Mn–Ti–O inclusions in the weld metal led to the refinement of the microstructure by detaining columnar grain growth. The complex inclusion exhibited the formation of  $\text{Ti}_2\text{O}_3$ ,  $\text{Ti}_3\text{O}_5$ , and  $\text{MnTi}_2\text{O}_5$  compounds that aided in grain refinement. During the solidification of the weldment, the  $\text{MnTi}_2\text{O}_5$  content increased leading to a manganese-depleted zone in the weld promoting nucleation and intergranular formation [26]. Therefore, the complex inclusions formed with a turbulent flow by added nanoparticles improved acicular ferrite content, refinement of grains and intergranular nucleation, which resulted in better properties.

Apart from the complex inclusion and turbulent flow, the recovered element Mn precipitated on the grain boundaries weakening the nucleation of bainite formation, thereby resulting in the formation of acicular ferrite. This occurred only with hardened elements (i.e. Vanadium, Ti, and Nitrogen) while cooling [30].

Hence, the studies clearly show that nanoparticle addition through electrode coating in the GMAW process improve stable microstructural formations in steel weld metal. Moreover, the nanoparticles aid in the recovery of elements, thereby forming complex inclusions, as well as increase the solidification time by the compounds. This nanoparticle addition assisted grain refinement and acicular ferrite formation with the significant effect by the quantity of nanoparticles added.



**Fig. 3.** Hardness in the low carbon weld metal with varying content of TiO<sub>2</sub> nanoparticles. Replotted from M. Fattahi, N. Nabhani, M. G. Hosseini, N. Arabian and E. Rahimi // *Micron* **45** (2013). (c) 2013 Elsevier B.V.

## 5. EFFECT OF NANOPARTICLE-COATED ELECTRODE ON THE WELD METAL MECHANICAL PROPERTIES

Previous sections showed that nanomaterial inserted into the weld through a welding electrode resulted in better microstructural formation and refinement of grains, which could lead to improved weld properties. Studies show that the refinement of grains could increase the hardness and tensile strength of the joint [31,32]. Fine-grain formation through nanoparticles could provide higher strength compared to the welded joints with no added nanoparticles.

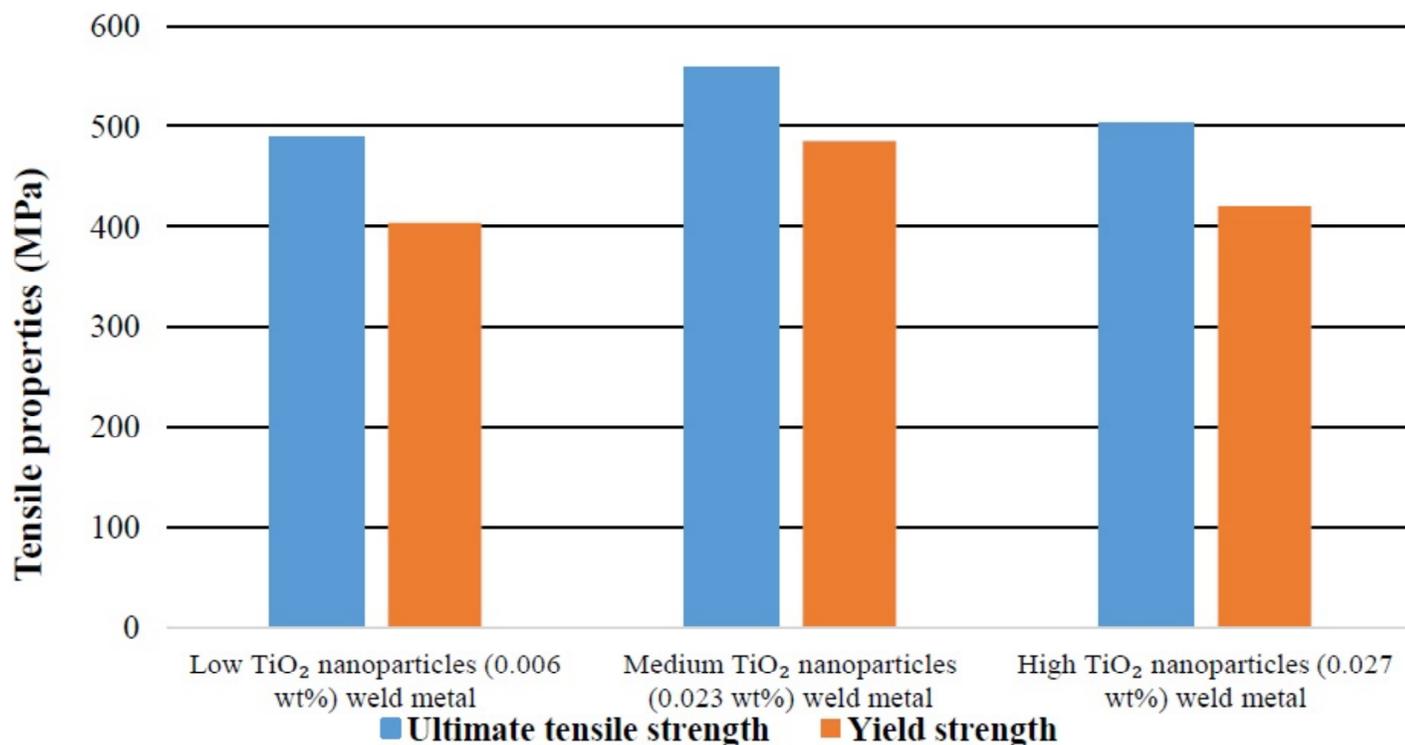
### 5.1. Hardness

Hardness property is an essential characteristic in the joint strength. If the hardness value in the weld region increases above the nominal level corresponding to the base metal, the weld impact strength is reduced and leads to the occurrence of brittle fracture or crack propagation. However, if the hardness value of the weld increases uniformly corresponding to the level of the base metal, the joint exhibits better integrity and performance. Research showed that the weld metal with increasing nanoparticle addition by coating on the base metal provided escalation in the hardness values [3,33]. This hardness improvement was also observed in the experiment by Fattahi et al. [19] on welding low-carbon steel with the TiO<sub>2</sub> nano-coated electrode, which was due to the grain refinement in the microstruc-

ture. Moreover, the hardness value increased by increasing the amount of TiO<sub>2</sub> nanoparticles in the electrode, shown in Fig. 3. This hardness increment was due to the increase of acicular ferrite content in microstructural formation.

In some cases, welds with increasing contents of nanoparticles gradually increased their hardness value, but, after attaining a sustainable value, the hardness value started to decrease even though further increasing the amount of nanoparticles added into the weld. This effect was observed in welding low-carbon steel with TiO<sub>2</sub> nanoparticles showing that the hardness increased with an increasing TiO<sub>2</sub> nanoparticle content in the electrode coating and decreased gradually. In addition, the hardness value decreased gradually from the columnar zone to the reheated zone, which may be due to the change in the microstructure and the grain size. However, the weld formed with a medium content of TiO<sub>2</sub> nanoparticles exhibited the highest hardness compared to the other weld metals formed with low and high contents of TiO<sub>2</sub> nanoparticles [18]. The similar phenomenon was also observed in the experiment by Chen et al. [17] on low-carbon steel with nano-marble addition (i.e. CaCO<sub>3</sub>) in the electrode. This decrease in hardness in both studies could be due to the size factor. The increment in the hardness value was due to the significant formation of acicular ferrite in the steel weld metal [18].

Thus, studies show that the hardness of the weld formed with added nanoparticles through the electrode coating increases with the nanoparticle content. This hardness increase is due to acicular fer-



**Fig. 4.** Tensile properties formed in the low carbon steel weld metals by varying TiO<sub>2</sub> nanoparticles content in electrode. Replotted from M. Fattahi, N. Nabhani, M. R. Vaezi and E. Rahimi // *Materials Science and Engineering: A* **528** (2011) 27. (c) 2011 Elsevier B.V.

rite in the microstructure. However, studies also show that increasing the amount of nanoparticles added increases hardness to a sustainable level, after which it decreases gradually, which is due to the nanomaterial size factor.

## 5.2. Tensile and impact properties

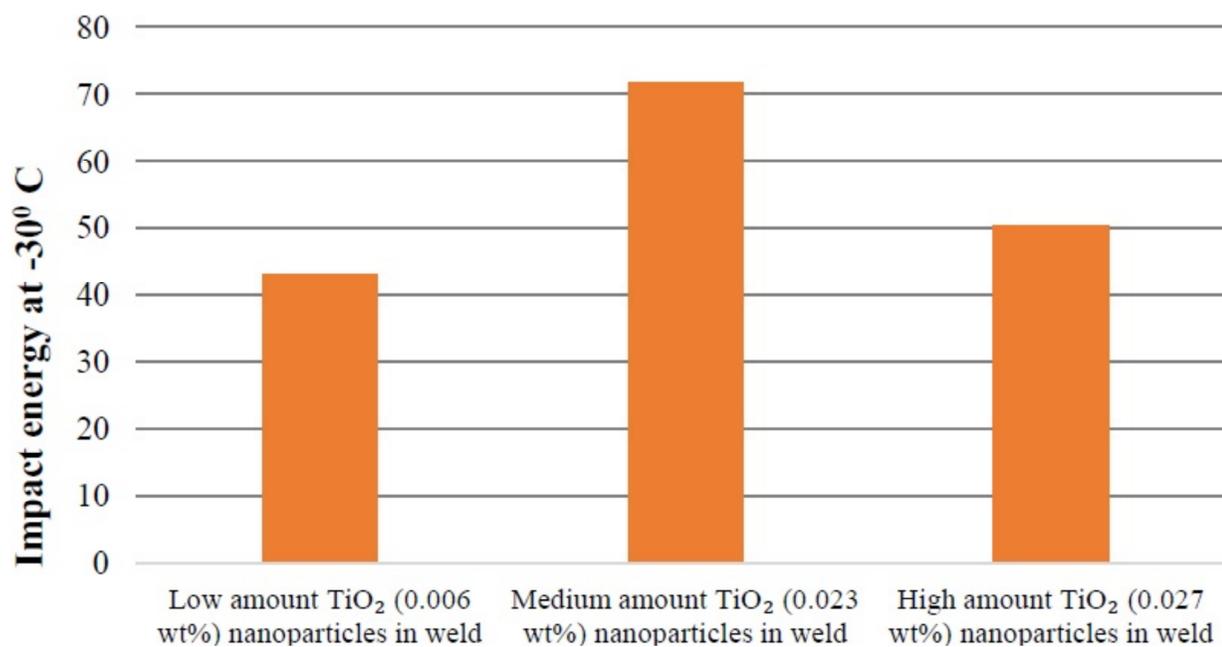
A previous study showed that TiO<sub>2</sub> nanoparticles added as an alloying element improved the tensile strength in C–Mn steels [34]. The weld formed with nanoparticles added through an electrode coating also improved the yield strength by the refinement of grains. Research on welding carbon steel with added TiO<sub>2</sub> nanoparticles in the electrode showed that the weld composition exhibited the recovery of elements, which aided in the lowering of temperature, resulting in grain refinement and improving tensile strength [15]. To identify the factors that improved the tensile strength, the experiment by Fattahi et al. [19] on welding low-carbon steel with a TiO<sub>2</sub> nanoparticle-coated electrode obtained welds with improved tensile and yield strength by an increased TiO<sub>2</sub> content in the electrode. The study concluded that the improvement in the strength mainly resulted from the improved grain size due to the refinement and increased acicular ferrite content in the microstructure.

The study by Fattahi et al. [18] showed that with the medium content of TiO<sub>2</sub> nanoparticles in the electrode exhibits more yield and ultimate tensile strength compared to other weld metals formed with low and high TiO<sub>2</sub> nanoparticle contents, shown in

Fig. 4. Earlier studies proved that the reduction in grain size by grain refinement would assist in increasing the tensile strength [35]. Therefore, the increased tensile strength was due to the reduced grain size, a greater amount of acicular ferrite and columnar zone reduction in the weld [18]. The decreased tensile properties in the weld metal formed by a high content of TiO<sub>2</sub> nanoparticles in the electrode were due to the increased oxygen content, increased allotriomorphic ferrite grain boundary and decreased columnar zone grain size.

Apart from the tensile strength, the impact toughness also increased with the content of nanoparticles in the weld metal. This was stated in the study by Fattahi et al. [19] showing that an improvement in the impact strength increased with increased acicular ferrite content and grain refinement in the weld metal. Previous research showed a relation between toughness and the dimple size, where the toughness improved with the decrease in the dimple sizes [36]. Moreover, the experiment by Pal and Maity [15] also agreed on the statement that toughness increased with an increased nanoparticle content. However, the reason for the improvement in the impact toughness was not only grain refinement, but also the oxygen and nitrogen level which was also one reason that was manipulated by the Ti content.

However, previous studies showed that a high oxygen content in the weld metal negatively influences the properties of the joint by reducing the toughness of the joint [37,38]. The experiment by Fattahi et al. [18] showed that the medium amount of TiO<sub>2</sub> nanoparticles in the electrode had higher



**Fig. 5.** Impact strength in the low carbon steel weld formed with varying content of TiO<sub>2</sub> nanoparticles electrode. Replotted from M. Fattahi, N. Nabhani, M. R. Vaezi and E. Rahimi // *Materials Science and Engineering: A* **528** (2011) 27. (c) 2011 Elsevier B.V.

toughness in the weld metal at -30 °C than the weld metals formed by low and high TiO<sub>2</sub> nanoparticle amounts in the electrode, which is shown in Fig. 5. So, the joint welded with the high TiO<sub>2</sub> nanoparticle content in the electrode had an increase in oxygen with an increase in the allotriomorphic ferrite content, which resulted in decreased impact strength. The low TiO<sub>2</sub> nanoparticle content exhibited a high Widmanstatten content in the weld, which deteriorated the impact strength of the joint. Research reported that cracks can be produced and propagated in the Widmanstatten ferrite, which is unfavourable for impact strength [32]. Hence, the reduction in the toughness strength in the weld metal was due to the increase in the oxygen content, variation in grain size, the amount of acicular ferrite, cleavages in the microstructures and inclusion characteristics [18].

Therefore, the nanoparticles added through electrode coating improved the tensile and yield strength. Increasing the nanoparticle content increased the tensile and yield strength by grain refinement in the weld. However, a significant increase in the nanoparticle content resulted in the reduction of tensile strength due to the oxygen content and columnar grain in the weld. In addition, the impact strength also decreased in the weld by the effect of oxygen with a significant increase in the nanoparticle content. However, a nominal level of nanoparticles in the weld increased the impact strength.

### 5.3. Corrosion resistance

The corrosion resistance property is an important characteristic for welds, used in corrosive environ-

ments. It has been shown that the weld formed by nanoparticles added through coating on the base metal improved the properties. For the case of electrode coating, the experiment by Fattahi et al. [10] on welding low-carbon steel with the addition of TiO<sub>2</sub> nanoparticles in the electrode decreased corrosion resistance at the grain boundaries and around the Ti-based inclusions of the weld metal. This was attributed to the non-metallic inclusions into the weld metal that act as a pitting agent for corrosion [39]. The difference in the alloying element concentration at the grain boundaries results in more corrosion at the grain boundaries in the weld metal. In addition, increasing the TiO<sub>2</sub> nanoparticles in the weld metal leads to an increase in the formation of a manganese-depleted zone around the Ti-based inclusion. This can result in the destruction of carbon steels due to reduced corrosion resistance along the manganese-depleted zone, when the weld is subjected to environments containing Cl [40]. However, the weld metal without added Ti nanoparticles showed the lowest corrosion rate [10]. Thus, TiO<sub>2</sub> addition is not suitable for improving the corrosion resistance property in low-carbon weld metal.

### 5.4. Wear resistance

Wear resistance also plays an important role in the integrity of the joint, if the joint is subjected to a friction environment. Welding low-carbon steel with the addition of nano-marble (i.e. CaCO<sub>3</sub>) in the welding electrode showed an increase in the wear resistance with the increase of the nano-marble content in the electrode, which was estimated by the weight loss, as shown in Table 1. However, the weld formed

**Table 1.** Abrasion wear loss varies by the nano-marble content in the low carbon steel weld metal . Based on data from B. Chen, F. Han, Y. Huang, K. Lu, Y. Liu and L. Li // *Welding Journal* 88 (2009) 5. (c) 2009 American Welding Society.

| Electrode with CaCO <sub>3</sub> nano-marbles addition (%)<br>in flux welded in low carbon steel | Abrasion weight loss, (g) |
|--|---------------------------|
| Electrode 1 – 0% - Weld metal 1  | 0.021                     |
| Electrode 2 – 10% - Weld metal 2   | 0.018                     |
| Electrode 3 – 20% - Weld metal 3   | 0.008                     |
| Electrode 4 – 25% - Weld metal 4   | 0.005                     |
| Electrode 5 – 50% - Weld metal 5   | 0.011                     |
| Electrode 6 – 100% - Weld metal 6  | 0.016                     |

with a nominal level of nano-marble exhibited higher wear resistance compared to the weld formed with the highest content of nano-marble [17]. The reasons for the improvement in wear resistance are yet to be examined.

Thus, nanomaterial in the welding electrode coating showed improvement in the properties. Moreover, wear resistance reduced the weight loss through the increasing content of nanomaterial in the welding electrode.

## 6. NANOMATERIALS USED AS FILLER MATERIALS IN GTAW PROCESS

The chemical composition of the filler metal is one of the determining factors for the formation of the microstructure and properties in the weld. The selection of filler metal is mostly done based on the composition of the base metals [31]. Studies have shown that the small particles used in the filler electrode improve the weld strength. The uniform distribution of particles is also required in filler metal fabrication. The filler material can be in various forms, such as powders, layers and wires. However, the selection of a filler should be adaptable to the welding process. For the non-consumable electrode in arc welding processes (i.e. GTAW), the usage of appropriate filler metal in the joint improves the microstructure as well as the joint properties. As studies maintained that the usage of small particles have an immense effect, the nanomaterials were added as an alloying element when manufacturing filler materials. The filler metals fabricated with nanomaterials had a uniform dispersion within the filler metal and to the weld formation, which also provided improvement in the properties [41]. The uniform dispersion ensured uniform cooling and microstructural formations in the weld metal, which in

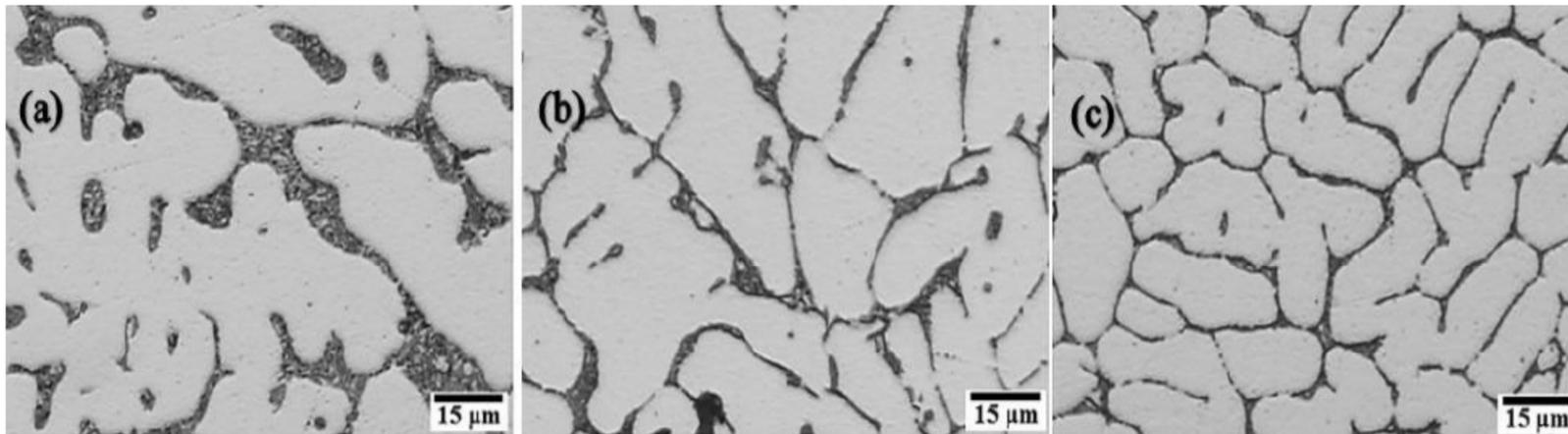
turn would form better properties in the weld metal [42]. Some of the nanoparticles added in the filler metals were metal oxides, noble metals and carbide particles.

Research showed that the carbonaceous element used as a reinforcing element in Al alloys exhibited a remarkable improvement in the properties and the refinement of grains [43]. This carbonaceous element could be used in filler metal for welding Al metals to improve the properties of the joint. The carbonaceous nanomaterials such as GNS and CNT, improve the properties by manipulating the grain growth. The GNS is the structural basic element for the CNT. Hence, if the GNS inclusion improves the properties of the Al metal, then CNT would be showing a better improvement of the properties.

Recently introduced in welding, composite filler wires containing nanoparticles significantly improve the properties of the joint. The composite filler metals also reduce defect formations. Moreover, the composite filler metals formed with small-sized particles (such as microparticles and nanoparticles) improve the properties of the joint [44]. The following section describes the effect of nanomaterial added fillers in the GTAW welding process.

### 6.1. Effect of filler metal with nanomaterial on defects

Research has shown that the nanoparticles included while alloying improves microstructural formation and reduces defects. Nanoparticle addition with uniform dispersion in the filler metal showed a reduction in the defects of the weld metal. Fattahi et al. [2] observed defect formation, such as a lack of penetration and coarse micro-porosity in the weld formed by filler metal without nanomaterial. The weld formed with MWCNT filler metal exhibited reduced defects and, yet, increased fine micro-porosity in the weld.



**Fig. 6.** Weld microstructures of 6061 Al alloys formed (a) without, (b) by 2.5 wt.%, and (c) by 5 wt.% of TiC nanoparticles. Reprinted with permission from M. Fattahi, M. Mohammady, N. Sajjadi, M. Honarmand, Y. Fattahi and S. Akhavan // *Journal of Materials Processing Technology* **217** (2015). (c) 2015 Elsevier B.V.

MWCNT filler metal also improved weld penetration and the appearance of the weld seam by decreasing the fluidity of the liquid weld metal.

The accumulations of nanoparticles in the weld led to negative effects such as defect formations and degradation of properties. This occurred in the experiment of Fattahi et al. [45] showing that the micro-crack formations by the cluster of GNS particle formation result in insufficient bonding with Al. Moreover, a large cluster of nanoparticle formation resulted in easy propagation of cracks. However, a higher content of GNS in the weld metal with uniform dispersion reduces discontinuity formation. Therefore, carbonaceous nanoparticles added through filler metal reduced discontinuity formation; however, the accumulation of particles has to be considered to reduce the negative effects on the joint [46,47]. Some of the factors influencing the microstructure of Al by the addition of MWCNT were dispersion of MWCNT in Al, material deformation and interfacial reaction between Al and MWCNT.

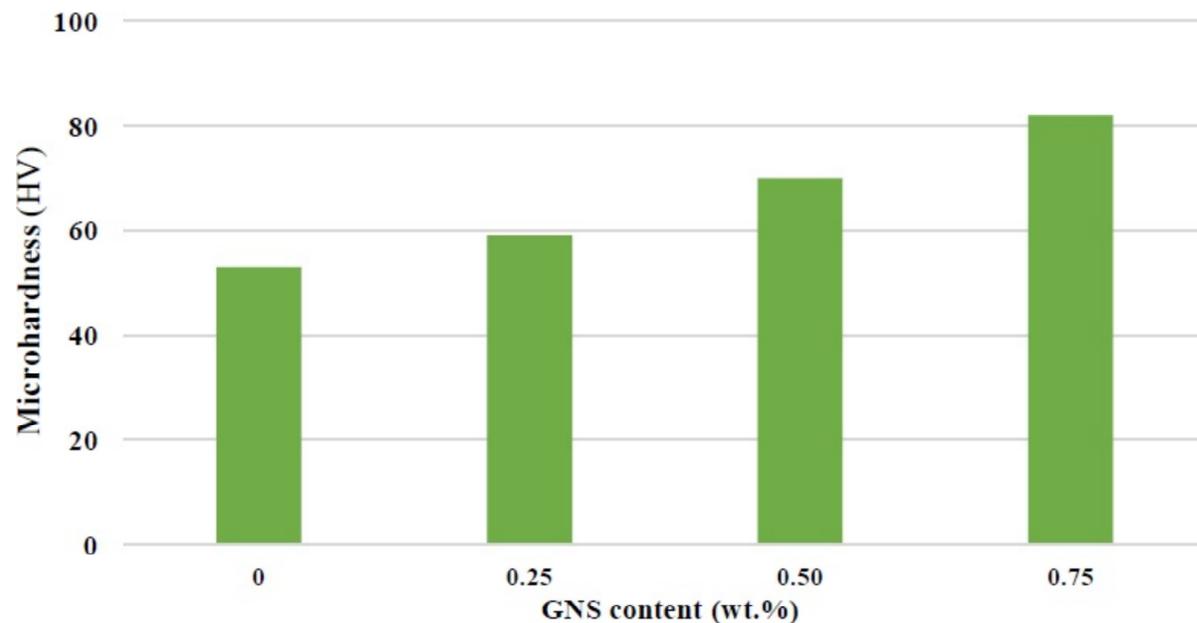
## 6.2. Effects of filler metal with nanomaterials on microstructure

Welding of Al with the filler metal containing MWCNT resulted in a weld with improved microstructural stability, thereby leading to improved joint strength [2]. This was due to grain refinement by the pinning effect at the grain boundaries [48]. Moreover, welding Al with GNS in the filler metal showed variation in the weld metal microstructure formed with and without GNS in the filler metal. The weld metal formed without added nanomaterial exhibited dendritic and equiaxed  $\alpha$ -Al grains and Al-Si eutectic phases; however, the weld formed with GNS addition in the filler metal only showed equiaxed  $\alpha$ -Al grains. This microstructural change occurred by the addition of GNS due to its heterogeneous nucleation site, the

pinning effect of GNS on the grain boundaries and deceleration of grain growth. Moreover, increasing the content of GNS in the filler metal resulted in fine equiaxed grains on the weld metal [45]. Carbonaceous nanoparticles in the filler metal improved the weld microstructure through grain refinement and transformed the microstructural phases into similar phases.

As carbonaceous nanoparticles showed grain refinement in the Al weld metal, it is anticipated that the TiC nanoparticles would provide better refinement and improvement in properties. The reason for choosing TiC nanoparticles instead of other nanoparticles for welding Al alloys is their low density and the good wear resistance and weldability provided. Research also showed the Al alloys with TiC nanoparticles as an alloying element in the alloy improved the mechanical properties by fine grain refinement [49]. Welding Al alloys with TiC nanoparticles as filler material improved the microstructure with grain uniformity and reduced grain growth. Grain refinements in the weld were improved by the pinning effect of TiC nanoparticles on the boundaries and the nucleation of TiC nanoparticles. This pinning effect occurred by the decreased primary  $\alpha$ -Al grain size by the increased volume fraction of TiC nanoparticles. Therefore, increasing the TiC nanoparticle content in the filler metal reduced the grain size and improved grain refinement, which is shown in Fig. 6. Nucleation site formation was enhanced by the lattice mismatch between Al and TiC nanoparticles [41].

Therefore, both the carbonaceous nanoparticles and ceramic nanoparticles in the filler metal resulted in welds with refined microstructures. In addition, both the weld formed with carbonaceous and ceramic nanoparticles led to grain refinement by the pinning and nucleation effect at the grain bound-



**Fig. 7.** Microhardness of the 6061 Al alloy weld metal by varying GNS content in filler metal. Replotted from M. Fattahi, A. R. Gholami, A. Eynalvandpour, E. Ahmadi, Y. Fattahi and S. Akhavan // *Micron* **64** (2014). (c) 2014 Elsevier B.V.

aries. Moreover, increasing the nanoparticle content in the filler metal increased fine grain refinement.

### 6.3. Effects of filler metal with nanomaterials on mechanical weld properties

The carbonaceous and ceramic nanoparticles in the filler metal produced refinement in the microstructure, which would improve hardness and tensile strength. Research has shown that small grain size formed in the weld metal increases the hardness and the tensile strength of the joint.

### 6.4. Hardness

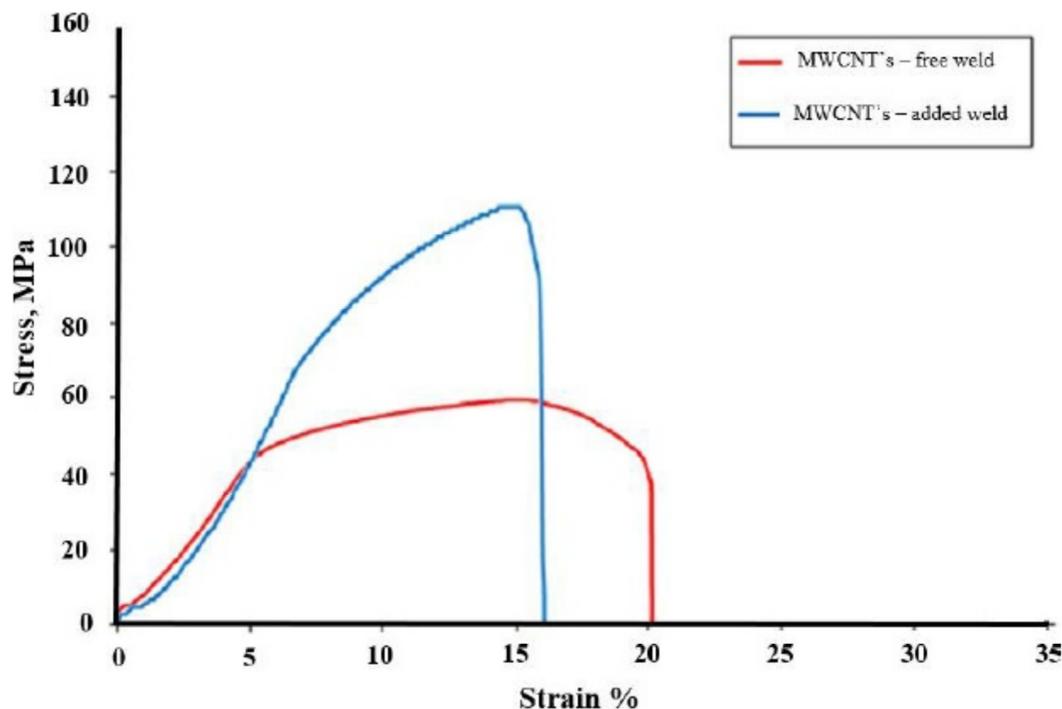
Research showed that the decrease in the grain size increases the hardness of the metal. The carbonaceous nanoparticles (i.e. MWCNT) added in the electrode with Al weld metal exhibited reduced grain size, which resulted in increased hardness. Moreover, there was another factor that increased hardness, namely, the formation of Al carbide ( $Al_4C_3$ ) influencing the rate of cooling in the weld metal [2]. This was also reported in the experiment by Fattahi et al. [45] on welding Al alloys with GNS in the filler metal. The reason for the increase in hardness was the same, but there was yet another reason, namely, the increase of dislocation density. Moreover, increasing the GNS content in the filler metal increased the microhardness in the weld metal, which is shown in Fig. 7. However, the weld metal formed by the filler metal without added nanomaterial showed hardness below the base metal hardness. This decrease was due to the increased temperature above the recrystallisation of the metal [2]. The

reasons for the improvement of hardness were grain refinement, increase of dislocation density and formation of aluminium carbide. Grain refinement was caused by an increased volume fraction at the grain boundaries through nanomaterial addition. The dislocation density increased in the weld metal by a difference in the thermal expansion of Al and GNS or MWCNT. Lastly, the carbonaceous element exhibited Al carbide formation while microstructural formation through easy bonding between elements [45].

When ceramic nanoparticles (TiC) were added in the filler metal, the weld showed increased grain refinement, thereby leading to improvement in the hardness of the Al weld joint. Moreover, weld hardness increased with an increase in the TiC nanoparticle content in the filler metal [41]. Two other factors increased the joint hardness: Firstly, the reduced grain size of the  $\alpha$ -Al enhanced the hardness by the decreased grain size. Another reason for increased hardness was the difference in the thermal coefficient of expansion between the Al and TiC nanoparticles, thereby producing thermal strains. Hardness, however, reduced at the HAZ, which was due to the grain growth and recrystallization along the joint [41].

Therefore, either carbonaceous or ceramic nanoparticles in the filler metal increased the hardness in the weld metal. Increasing the content of nanoparticles improved the hardness properties. The reasons for the increase in hardness are same for both the nanoparticles:

1. Reduction in grain size,
2. Formation of aluminium carbide ( $Al_4C_3$ ) and
3. Increased dislocation density (this occurred only in TiC and GNS).



**Fig. 8.** Stress vs Strain curve for the 1050 Al alloy weld metals with/without nanomaterial addition. Reprinted with permission from M. Fattahi, N. Nabhani, E. Rashidkhani, Y. Fattahi, S. Akhavan and N. Arabian // *Micron* **54-55** (2013). (c) 2013 Elsevier B.V.

### 6.5. Tensile property

For the case of tensile strength, the Al alloy joint formed with MWCNT added in the filler metal improved the ultimate tensile strength with reasonable ductility compared to the other weld metal, as shown in Fig. 8, [2]. The increase in tensile strength was due to the thermal expansion difference between Al and MWCNT. In addition, the grain refinement and uniform dispersion of MWCNT were also important factors for the improvement of the tensile strength.

Moreover, the addition of GNS in the filler metal also improved the ultimate tensile and yield strength of the Al weld metal, due to the uniform distribution and unique properties of GNS. The uniform dispersion of GNS restricts the dislocation motion, thereby strengthening the Al joint. Moreover, the improvement of tensile strength was also aided by grain refinement, which occurred by the fine grains disrupting the dislocation movement. This disruption led to an increasing dislocation density with uniform grain boundaries that improved the rate of strain hardening [45].

Ceramic nanoparticles (i.e. TiC) added to the filler metal produced increased ultimate tensile strength and yield strength and, yet, reduced elongation. This improvement was due to three reasons: Firstly, the thermal mismatch between the TiC nanoparticles and Al could increase the dislocation density in the weld, which increases the tensile strength. Secondly, the decreased grain size by grain refinement improved the tensile strength. Thirdly, dislocation movement was obstructed by the fine TiC particles, thereby increasing the tensile strength of the joint.

Moreover, the fracture surface showed ductile fracture by the dimples formed. The weld fractured with 5 wt.% of TiC nanoparticles showed fine and uniform dimples compared to the weld formed with 2.5 wt.% of TiC nanoparticles and without nanoparticles in the filler metal [41].

Hence, the weld tensile strength increased with the filler metal consisting of carbonaceous (i.e. MWCNT and GNS) or ceramic nanoparticles (i.e. TiC); however, elongation decreased. The reasons for the improvement of the weld were

1. Uniform dispersion of nanoparticles,
2. Grain refinement and
3. Properties of nanoparticles added in the filler metal.

### 7. CONCLUSIONS

Installation and structures are designed with high-strength materials for increased stability and long life. But during manufacturing, processes like forming, machining and welding reduce the material strength, thereby degrading the material properties. Specially, GTAW and GMAW processes degrade the strength of the material at the joining regions due to, for example, the heat input, dilution factor and filler metal addition. When added to the filler metals and electrode coating, proper nanomaterials in the joining region have compensated for these losses and improved their material strength and properties.

Overall, the introduction of nanomaterial to the joint produces

- Reduction of weld defects, such as base metal pores and crack initiation occurring by non-uniform shrinkage with uniformly distributed nanoparticles. However, an inappropriate selection of nanoparticles and joint design results in void formations in the weld.
- Reduction of grain size in the microstructure. When adding the proper size and uniform distribution of nanoparticles increases the pinning effect on grain boundary and grain nucleation during welding.
- Stable microstructural formation. In order to improve particular properties, a specific phase in the microstructure needs to be increased, which is obtained by appropriate nanoparticle addition and with a specific quantity of nanomaterial.
- Improvement of joint mechanical properties. Hardness is improved through uniform nanoparticle distribution leading to uniform heat input and dissipation. However, nanoparticle accumulation results in non-uniform hardness. Tensile strength improved through fine microstructural formation by the appropriate selection of nanoparticles and their characteristics.
- Improved corrosion resistance and wear resistance, which can be achieved by a suitable addition of nanoparticles in accordance with the base material, as well as the fine microstructure by the uniform dispersion and nominal quantity of nanomaterial added.

These improvements have been influenced by the main factors such as the uniform dispersion of nanoparticles, selection of nanomaterials based on their characteristics and the quantity as well as the size of the nanoparticles. Welding with nanomaterial added has been mostly executed by nanopowders and the nano-carbonaceous element. Metal oxides, ceramic carbides and rare element oxide nanopowders are mostly used in weld production. In the case of nano-carbonaceous elements, CNT and GNS have been used.

In welding, the effect of nanoparticles modifies the physics of the joining region, thereby resulting in significant improvement in the welding region with a stable microstructure and properties. However, nanomaterials have been significantly used in weld production to improve material strength. Research is being conducted to achieve high joint integrity in various metals using various welding processes such as friction stir welding, GTAW, GMAW and laser beam welding. More research is still being conducted on improving the joint efficiency in dissimilar welding through nanoparticles added.

## REFERENCES

- [1] L. Wolfgang, *Industrial application of nanomaterials - Chances and risks : Technology analysis* (Dusseldorf: Future Technologies Division of VDI Technologiezentrum, 2004).
- [2] M. Fattahi, N. Nabhani, E. Rashidkhani, Y. Fattahi, S. Akhavan and N. Arabian // *Micron* **54-55** (2013) 28.
- [3] M. Ishak, K. Maekawa and K. Yamasaki // *Materials Science and Engineering: A* **536** (2012) 143.
- [4] A.M. Orishich, A.G. Malikov and A.N. Cherepanov // *Physics Procedia* **56** (2014) 507.
- [5] D. Wolfgang and A. Dorfen, *Introduction of nanoparticles*, United States of America Patent 8,240,544 B2, 14 August 2012.
- [6] V.F. Puentes, K.M. Krishnan and A.P. Alivisatos // *Science* **291** (2001) 2115.
- [7] M. A. Kuznetsov and E. A. Zernin // *Welding International* **26** (2011) 311.
- [8] L.-E. Svensson // *Svetsaren* **54** (1999) 29.
- [9] D. Widgery, L. Karlsson, M. Muruganath and E. Keehan, In: *Proceedings of 2nd International Symposium on High Strength Steel* (Belgium, 2002), p. 117.
- [10] M. Fattahi, N. Nabhani, E. Rafiee, M. Nasibi, E. Ahmadi and Y. Fattahi // *Materials Chemistry and Physics* **146** (2014) 105.
- [11] I. Watanabe and T. Kojima // *Journal of the Japan Welding Society* **49** (1980) 1158.
- [12] N. Mori, H. Homma, S. Ohkita and M. Wakabayashi, *Mechanisms of Notch Toughness Improvement in Ti-B Bearing Weld Metal* (IIW Doc, 1981), p. 1196.
- [13] T. Koseki and G. Thewlis // *Materials Science and Technology* **21** (2005) 867.
- [14] P. Marcus, In: *Corrosion Mechanisms in Theory and Practice, 2nd ed.* (New York: CRC Press, 2002), p. 243.
- [15] T. K. Pal and U. K. Maity // *Materials Sciences and Applications* **2** (2011) 1285.
- [16] C. Chen, H. Xue, H. Peng, L. Yan, L. Zhi and S. Wang // *Journal of Nanomaterials* **2014** (2014) 1.
- [17] B. Chen, F. Han, Y. Huang, K. Lu, Y. Liu and L. Li // *Welding Journal* **88** (2009) 99.
- [18] M. Fattahi, N. Nabhani, M. R. Vaezi and E. Rahimi // *Materials Science and Engineering: A* **528** (2011) 8031.

- [19] M. Fattahi, N. Nabhani, M. G. Hosseini, N. Arabian and E. Rahim // *Micron* **45** (2013) 107.
- [20] X. J. Zhuo, Y. Q. Wang, X. Wang and H. Lee // *Journal of Iron and Steel Research, International* **17** (2010) 10.1
- [21] S. A. David and T. DebRoy // *Science* **257** (1992) 49.
- [22] J. Byun, J. Shim, J. Suh, Y. Oh, Y. Cho, J. Shim and D. Lee // *Materials Science and Engineering: A* **319-321** (2001) 326.
- [23] T. Pan, Z. Yang, C. Zhang, B. Bai and H. Fang // *Materials Science and Engineering: A* **438-440** (2006) 1128.
- [24] C. Wang, M. Wang, J. Shi, W. Hui and H. Dong // *Scripta Materialia* **58** (2008) 492.
- [25] J. Byun, J. Shim and Y. Cho // *Scripta Materialia* **48** (2003) 449.
- [26] J. S. Byun, J. Shim, Y. Cho and D. Lee // *Acta Materialia* **51** (2003) 1593.
- [27] S. S. Babu // *Current Opinion in Solid State and Materials Science* **8** (2004) 267.
- [28] N. A. Fleck, Ø. Grong, G. R. Edwards and D. K. Matlock // *Welding Journal* **65** (1986) 113.
- [29] Z. Huang and M. Yao // *Materials Science and Engineering: A* **119** (1989) 211.
- [30] T. Furuhashi, J. Yamaguchi, N. Sugita, G. Miyamoto and T. Maki // *ISIJ International* **43** (2003) 1630.
- [31] ASM International Handbook committee, *Metals Handbook: Welding, brazing, and soldering* (Metals Park: American Society for Metals, 1993).
- [32] L.-E. Svensson, In: *Control of Microstructures and Properties in Steel Arc Welds* (Florida: CRC Press, 1993), p. 163.
- [33] K. Tseng and P. Lin // *Materials* **7** (2014) 4755.
- [34] S. Hossein Nedjad, Y. Zahedi Moghaddam, A. Mamdouh Vazirabadi, H. Shirazi and M. Nili-Ahmadabadi // *Materials Science and Engineering: A* **528** (2011) 1521.
- [35] H. Bhadeshia and R. Honeycombe, In: *Steels: Microstructure and Properties* (Bulinton, Elsevier Limited, 2003), p. 27.
- [36] O. A. Hilders and M. Santana // *Metallography* **21** (1988) 151.
- [37] S. Terashima and H. K. Bhadeshia // *Science and Technology of Welding and Joining* **11** (2006) 580.
- [38] S. Terashima and H. K. Bhadeshia // *Science and Technology of Welding and Joining* **11** (2006) 506.
- [39] M. A. Baker and J. E. Castle // *Corrosion Science* **34** (1993) 667.
- [40] M. A. Baker and J. E. Castle // *Corrosion Science* **33** (1992) 1295.
- [41] M. Fattahi, M. Mohammady, N. Sajjadi, M. Honarmand, Y. Fattahi and S. Akhavan // *Journal of Materials Processing Technology* **217** (2015) 21.
- [42] S. Kou, *Welding Metallurgy, 2nd ed.* (New York: John Wiley & Sons, 2003).
- [43] F. H. Latief, E. S. M. Sherif, A. A. Almajid and H. Junaedi // *Journal of Analytical and Applied Pyrolysis* **92** (2011) 485.
- [44] X. Li, H. Choi and D. Wiess, *Nanocomposite welding wires*, United states Patent US 20140197147A1, 17 July 2014.
- [45] M. Fattahi, A. R. Gholami, A. Eynalvandpour, E. Ahmadi, Y. Fattahi and S. Akhavan // *Micron* **64** (2014) 20.
- [46] S. R. Bakshi and A. B. Agarwal // *Carbon* **49** (2011) 533.
- [47] R. Pérez-Bustamante, F. Pérez-Bustamante, I. Estrada-Guel, L. Licea-Jiménez, M. Miki-Yoshida and R. Martínez-Sánchez // *Materials Characterization* **75** (2013) 13.
- [48] T. Laha, Y. Chen, D. Lahiri and A. B. Agarwal // *Composites Part A: Applied Science and Manufacturing* **40** (2009) 589.
- [49] W. Kim and Y. Yu // *Scripta Materialia* **72-73** (2014) 25.